

PROCEEDINGS
OF THE
INDIAN ACADEMY OF SCIENCES

VOL. XVIII

SECTION A

BANGALORE CITY .
PRINTED AT THE BANGALORE PRESS, MYSORE ROAD
1944

CONTENTS

SECTION A—VOL. XVIII

No. 1—July 1943

	PAGE
Studies in Blue Perchromic Acid. Part I. Kinetics of the Decomposition of the Blue Perchromic Acid in Various Organic Media SATYA PRAKASH AND RAM CHANDRA RAI	1
Spectral and Collision Data of CO^+ and the Dissociation Energy of Carbon Monoxide R. K. ASUNDI	8
Some Integrals involving Humbert Function . . . B. R. PASRICHA	11
Dynamics of Thunderstorms S. L. MALURKAR	20
The Action of Grignard Reagents on Benzopyrones. Part I. Preparation of Some Chromenes from 4-Substituted Coumarins A. R. SUKUMARAN KARTHA AND K. N. MENON	28
Opacity Changes in Gel-Forming Mixtures during Setting. Part II. Thorium Phosphate, Cerium Phosphate, Thorium Arsenate and Stannic Phosphate Gels . . . T. V. DESAI AND S. GURUSWAMY	31
Excitation Processes in the Night Sky and the Aurora. TA-YOU WU	40
Optical Theory of Chromatic Emulsions and of the Christiansen Experiment G. N. RAMACHANDRAN	67

No. 2—August 1943

A Tauberian Theorem and Its Application to Convergence of Fourier Series K. S. K. IYENGAR	81
On Arithmetic Functions P. KESAVA MENON	88
Bacterial Chemotherapy, I: Synthesis of N^1 -Substituted Sulphanilamides S. RAJAGOPALAN	100
Bacterial Chemotherapy, II: Synthesis of Possible Intestinal Antiseptics of the Sulphanilamide Group . . . S. RAJAGOPALAN	104
Bacterial Chemotherapy, III: Synthesis of Possible Lipophilic Chemotherapeutics of the Sulphanilamide Group S. RAJAGOPALAN	108

	PAGE
New Convergence and Summability Tests for Fourier Series	K. S. K. IYENGAR 113
The Brightness of the Zenith Sky during Twilight—Part II	M. W. CHIPLONKAR AND J. D. RANADE 121

No. 3—September 1943

A Further Study of Atmospherics during the Monsoon Period	N. S. SUBBA RAO 127
A Study of 'Carpasemine' Isolated from <i>Carica papaya</i> Seeds	T. B. PANSE AND A. S. PARANJPE 140
Chemical Composition of <i>Calotropis gigantea</i> . Part I. Wax and Resin Components of the Latex	P. BHASKARA RAMA MURTI AND T. R. SESHADRI 145
Fixed Oil from <i>Jatropha curcas</i> (Linn.)	A. R. SUKUMARAN KARTHA AND K. N. MENON 160
The Condensation of Aldehydes with Malonic Acid. Part XV. Condensation of 5-Bromosalicylaldehyde and of 3: 5-Dibromosalicylaldehyde: Influence of Dissimilar Groups	KANTILAL C. PANDYA AND MISS RASHMI BALA K. PANDYA 164
Colorimetric Estimation of Boric Acid with Pentamethylquercetin	K. NEELAKANTAM AND S. RANGASWAMI 171

No. 4—October 1943

A Note on Poisson Distribution	K. SANKARA PILLAI 179
Fluctuations of Light Intensity in Coronæ formed by Diffraction	G. N. RAMACHANDRAN 190
Chemical Investigation of Indian Fruits. Part IV. A Note on the Bitter Principle of a Variety of <i>Citrus limetta</i>	T. R. SESHADRI 201
Pigments of Cotton Flowers. Part IX. A Note on the Occurrence of Populnetin in Indian Cotton Flowers	P. SURYAPRAKASA RAO AND T. R. SESHADRI 204
Chemical Examination of Indian Ergot of the Nilgiris	S. RANGASWAMI AND T. R. SESHADRI 206
Interferometric Studies of Light Scattering in Binary Liquid Mixtures: Part I	K. SUNANDA BAI 210

	PAGE
Activation of Nitrogen in the Presence of Mercury	
. S. S. JOSHI AND A. PURUSHOTHAM	218
Some Aspects of the Biogenesis of Anthoxanthins	
. P. SURYAPRAKASA RAO AND T. R. SESHADRI	222

No. 5—November 1943

Part I: GENERAL THEORY

The Vibration Spectrum of a Crystal Lattice	SIR C. V. RAMAN	237
Normal Oscillations of the Diamond Structure	S. BHAGAVANTAM	251
The Normal Vibrations in Some Typical Cubic Crystals		
. E. V. CHELAM	257	
Modes of Atomic Vibration in the Fourteen Bravais Lattices		
. G. N. RAMACHANDRAN	266	
Normal Vibrations of Crystal Lattices: Application of Group Theory	E. V. CHELAM	283

Part II: THE EXPERIMENTAL FACTS OF SPECTROSCOPY

Raman Spectra of Crystals and Their Interpretation		
. R. S. KRISHNAN	298	
Luminescence Spectra and Vibrations in Crystal Lattices		
. D. D. PANT	309	

Part III: DISCUSSION OF PARTICULAR CASES

Character Tables for the Atomic Vibrations in Some Cubic Crystals	E. V. CHELAM	327
The Frequency Spectrum of the Diamond Lattice	E. V. CHELAM	334
Modes of Vibration of the Hexagonal Close-Packed Lattice		
. G. N. RAMACHANDRAN	341	

No. 6—December 1943

On Maris and Hulburt's Ultraviolet Light Theory of Auroræ and Magnetic Storms	TA-YOU WU	345
Electrolytic Solution Pressure of Copper Wires under Strain		
. LAJJA RAM GAUTAM AND J. B. JHA	350	
Chemotherapy of Bacterial Infections. IX. Synthesis of Some Sulphathiazole Derivatives	K. GANAPATHI	355

Chemotherapy of Bacterial Infections. X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-Diacetsulphanilylamidothiazole. A New Route to Sulphathiazole	
. C. V. DELIWALA, K. GANAPATHI AND M. V. SHIRSAT	360
Fluorescence Reactions with Boric Acid and <i>o</i> -Hydroxy-Carbonyl Compounds, and Their Application in Analytical Chemistry.	
Part II. Detection of $\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ -\text{C}-\text{C}-\text{C}- \\ \quad \end{array}$ in Aromatic Compounds containing C, H and O only	
K. NEELAKANTAM, L. RAMACHANDRA ROW AND V. VENKATESWARLU	364
The Photo-Reduction of Ferric Chloride in Presence of Aqueous Acetone and Anhydrous Ether	
. MATA PRASAD AND P. R. BAVDEKAR	373

STUDIES IN BLUE PERCHROMIC ACID

Part I—Kinetics of the Decomposition of the Blue Perchromic Acid in Various Organic Media

BY SATYA PRAKASH, D.Sc., F.A.Sc.,

AND

RAM CHANDRA RAI, M.Sc.

(*University of Allahabad*)

Received April 30, 1943

BARRESWIL¹ observed in 1847, that a deep blue solution is produced when a concentrated solution of chromic acid is mixed with hydrogen peroxide. If ether be shaken up with the blue solution, the aqueous layer is decolourised, and the ethereal layer retains the blue product. It was further observed by Grosvenor² that the blue compound is also soluble in ethyl acetate, amyl chloride, and various amyl esters. It is insoluble in carbon disulphide, benzene, toluene, carbon disulphide and various oils. The ethereal solution gives dirty violet precipitates with various alkaloids and amines, and when the precipitates are dried and treated with acids and ether, the blue solution is again obtained. Berthelot,³ moreover, showed that with strong acids and a solution of dichromate, hydrogen peroxide gives the blue colour of the hypothetical blue perchromic acid. With the weaker acids, the colour is violet and not blue. The blue perchromic acid as extracted with ether or ethyl acetate is stable only for a few hours ; it decomposes with the evolution of oxygen. Various attempts have been made by Barreswil, Aschoff,⁴ Brodie,⁵ Martinon,⁶ Berthelot, Riesenfeld,⁷ Spitalsky⁸ and others to elucidate the nature of this blue perchromic acid. In spite of the extensive work of Riesenfeld and Spitalsky, on the catalytic decomposition, not much work has been done on the kinetics of the decomposition of the blue perchromic acid itself. In the present series of papers, we propose to undertake the study of this blue perchromic acid from various standpoints with an idea to work out the conditions under which the acid is produced, its stability and decompositions, and also the various organic reactions in which the acid may be used.

Preparation of the Blue Acid

In all the experiments recorded in this paper, the blue perchromic acid was prepared from potassium dichromate (5% solution), dilute sulphuric

acid (2 N) and hydrogen peroxide (1.8 N). These solutions, as well as ether, were cooled in ice. 80 c.c. of the dichromate solution were taken in Jena conical flasks, also cooled to the ice temperature, and to this solution were added 20 c.c. of the dilute sulphuric acid. 40 to 50 c.c. of the hydrogen peroxide solution were added to the mixture, and immediately, the reaction mixture was shaken with about 120 c.c. of the ice-cooled ether. The ethereal layer which extracted out the blue perchromic acid was separated out from the aqueous layer by separating funnel. The proper separation was very necessary in the study of the reactions and therefore, all care was taken to ensure it.

The concentration of the blue acid thus extracted depended on the mode of preparation and the quantity of hydrogen peroxide used. The concentrations of the acid were determined in terms of the iodine liberated from potassium iodide in presence of dilute sulphuric acid, the iodine being titrated with hypo (N/20). A known volume of the blue acid was also evaporated to dryness over water-bath, and the residue left was weighed. The residue was further ignited in the platinum crucible and also weighed.

For each set of experiments, the same blue perchromic acid was used for proper comparison. This is necessary, because each preparation of the blue perchromic acid gives the acid of different strengths and characteristics.

The decomposition of the blue acid follows the monomolecular formula, and therefore the velocity constants were determined by the use of the equation :

$$K = \frac{1}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log_{10} \frac{a}{a-x},$$

where a is the initial concentration, and $a - x$ the concentration at the time t .

Influence of Temperature on Decomposition

The 10 c.c. of the blue perchromic acid, prepared by the method given, left a residue of 0.0294 g. when evaporated over water-bath. This residue when ignited in the platinum crucible weighed 0.0198 g. of Cr_2O_3 .

Different portions of the same acid were allowed to stand in Jena conical flasks in thermostats maintained at 10° , 20° and $30^\circ \pm 0.2$. 2 c.c. of the blue acid were pipetted out from time to time, and immediately transferred to potassium iodide solution acidified with dilute sulphuric acid. The iodine liberated was titrated with hypo (N/20).

TABLE I

At 10°			At 20°			At 30°		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	4·2	0·000443	19	4·1	0·00148	0	4·15	0·00293
60	3·95	0·000659	39	3·7	0·00235	15	3·75	0·00560
120	3·5	0·000693	79	3·1	0·00210	30	2·8	0·00734
180	3·15	0·000670	109	2·65	0·00225	45	2·15	0·00736
240	2·9	0·000776	139	2·2	0·00225	60	1·5	0·00718
300	2·45	0·000807	169	1·85	0·00234	75	1·2	0·00737
360	2·15	0·000847	199	1·6	0·00222	90	0·9	0·00791
420	1·85	0·000960	229	1·3	0·00237	105	0·6	
480	1·45	0·00100	259	1·05	0·00251			
540	1·2	0·00100	289	0·85				
600	1·0							
Average K/2·303 Induction period		0·000923 300 mins.			0·00229 70 mins.			0·00743 40 mins.

The decomposition of blue perchromic acid is very slow at 0° C. ; it takes more than 20 hours to undergo decomposition. At lower temperatures there is a pronounced induction period, and therefore, the monomolecular values of K show also a slight continuous increase with time. At temperatures above 30°, the decomposition is very rapid. The values of $\log K$ plotted against inverse temperatures ($\frac{1}{T}$) give a straight line, showing that Arrhenius equation is applicable to the decomposition of the blue perchromic acid.

From the results recorded above, it is also seen that there is a marked induction period at low temperatures within which the values of K show a continuous increase.

Decomposition of the Blue Acid in Presence of Benzene

It is known that the blue perchromic acid is not extracted out by benzene, but benzene being miscible with ether, it was found interesting to study the decomposition of the acid in ethereal solution in presence of

benzene. The blue acid was prepared by mixing 80 c.c. of 5% potassium dichromate, 20 c.c. of 2 N sulphuric acid, 50 c.c. of 1.8 N hydrogen peroxide and 120 c.c. of ether. From the ethereal extract of the perchromic acid, the following four combinations were made, keeping the total volume 30 c.c. and maintaining the same concentration of the blue acid. The decompositions of these four combinations at 30° were studied as in the previous experiments.

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + benzene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + benzene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + benzene 10 c.c.

TABLE II

No benzene			2 c.c. benzene			6 c.c. benzene			10 c.c. benzene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	7·7	·01026	3	7·65	·01060	6	6·95	·01321	9	5·4	·0124
15	5·4	·00912	18	5·3	·00999	21	4·2	·0134	17·5	4·25	·0138
30	4·1	·00976	34	3·75	·01009	36	2·75	·0133	24	3·35	·0141
45	2·8	·00940	48	2·75	·00999	51	1·7	·0161	32	2·5	·0162
60	2·1	·00987	63	1·95	·01004	66	0·75	·0155	54	1·0	·0188
75	1·4	·00985	78	1·4	·01090	81	0·45	·0162	69	0·5	·0177
90	1·1	·00977	93	0·9	·01050	96	0·3		84	0·25	
105	0·75	·00985	108	0·6	·01040						
120	0·5		123	0·4							
Average K/2·303		·00973			·01031		I II	·0133 ·0159		I II	·0134 ·0175

It will be seen from the results recorded in Table II, that the decomposition of the blue acid is faster in presence of benzene than in ether alone. When the concentration of benzene is increased, it appears as if the decomposition is taking place in two stages : the monomolecular constants of the second stage are larger than those of the first stage. It is very likely that benzene reacts chemically with perchromic acid, and this secondary reaction influences the primary decomposition of the blue acid. The study of the

products formed by the reaction of benzene and perchromic acid is reserved for a subsequent paper.

Decomposition of the Blue Acid in Presence of Toluene

The decomposition kinetics of the blue perchromic acid was studied in presence of toluene also in the same way as in the previous case. The blue acid was prepared and extracted with ether, 10 c.c. of the acid on evaporation on water-bath left a residue of 0.0682 g., and this residue on ignition weighed 0.0448 g. of Cr_2O_3 . The decomposition of the following combinations was investigated at 30° C.:

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + toluene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + toluene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + toluene 10 c.c.

TABLE III

No toluene			2 c.c. toluene			6 c.c. toluene			10 c.c. toluene		
Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303
0	6.05		3	5.25		6	4.6		9	3.15	
15	4.35	.00899	18	3.9	.0086	21	2.6	.0165	14	2.35	.0254
30	2.95	.01040	33	2.3	.0119	36	1.25	.0188	24	1.45	.0224
45	2.2	.00974	48	1.6	.0115	51	0.65	.0188	29	0.95	.0260
60	1.6	.00962	63	0.9	.0123	66	0.45	.0168	39	0.55	.0252
75	1.15	.00961	78	0.65	.0120				44	0.45	.0241
90	0.75	.01000	93	0.5	.0113				54	0.3	.0271
Average K/2.303		.0097			.0118			.0177			.0250

From these results, it will be seen that monomolecular constants are obtained when the decomposition of perchromic acid takes place in the presence of toluene. With the increased concentrations of toluene, we get an increased value of K.

Decomposition of the Blue Acid in Presence of Xylene

The results on the decomposition kinetics of the blue perchromic acid in presence of xylene are given in Table IV. The blue acid was prepared

in the way already described. 10 c.c. of this acid when dried on water-bath left 0.058 g. of residue which on ignition gave 0.0387 g. of Cr_2O_3 . The decomposition of the following combinations was studied at 30° .

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + xylene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + xylene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + xylene 10 c.c.

TABLE IV

No xylene			2 c.c. xylene			6 c.c. xylene			10 c.c. xylene		
Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303	Time mins.	Hypo c.c.	K/2.303
0	4.9	·0077	3	4.4	·0079	6	4.2	·0097	9	2.9	·0281
15	3.75	·0077	18	3.35	·00877	21	3.0	·0107	14	2.1	·0308
30	2.85	·0087	33	2.4	·00862	36	2.0	·00931	24	1.0	·0308
45	2.15	·00906	48	1.8	·00882	51	1.6	·01003	29	0.7	·0286
60	1.4	·00931	63	1.3	·00910	66	1.05	·0096	39	0.4	·0281
75	1.1	·0087	78	0.9		81	0.8	·00938	44	0.3	
90	0.8					96	0.6				
Average K/2.303		·00892			·00875			·00976			·02928

In the presence of xylene, perchromic acid decomposition rate is increased. With 2 c.c. of xylene, the change observed is not marked, whereas with 10 c.c. of it, the rate of decomposition increases about three times.

It is very significant to see that the decomposition influence is most prominent in the case of xylene and the least in the presence of benzene. Toluene shows an intermediate behaviour as is shown in the following table:

TABLE V

Hydrocarbon			K_1 in absence of hydrocarbon	K_2 with 10 c.c. hydrocarbon	K_2/K_1
Benzene	·02241	·04030	1.79
Toluene	·02235	·05757	2.57
Xylene	·02054	·06747	3.28

We have observed that along with the decomposition of perchromic acid, traces of aldehydes are formed from toluene and xylene, which give indication with Schiff's reagent. We are also studying the decomposition products of the blue acid.

Summary

The decomposition kinetics of the blue perchromic acid was studied under various conditions. The decomposition reaction is monomolecular. The value of K at 10° is 0.002125, at 20° 0.005273 and at 30° 0.01711 to 0.02241. The values differ slightly with different preparations. The values of $\log K$ plotted against $1/T$ give straight line, showing that Arrhenius equation is valid. From the study of kinetics, we find that there is a marked induction period also.

The rate of decomposition of the blue acid is markedly increased in the presence of benzene, toluene and xylene. When these hydrocarbons are present to the extent of 33 per cent. of the ethereal solution, the values of K increase 1.79 times with benzene, 2.57 times with toluene and 3.28 times with xylene, when the temperature maintained is 30° .

REFERENCES

1. Barreswil .. *Ann. Chim. Phys.*, 1848, **20** (3), 364 ; *Compt. Rend.*, 1848, **16**, 1085.
2. Grosvenor .. *J. Amer. Chem. Soc.*, 1895, **17**, 41.
3. Berthelot .. *Compt. Rend.*, 1889, **108**, 24, 157, 477.
4. Aschoff .. *Chem. News*, 1862, **5**, 129 ; *J. prakt. Chem.*, 1860, **81** (1), 402.
5. Brodie .. *Proc. Roy. Soc.* 1861, **11**, 443.
6. Martinon .. *Bull. Soc. Chim.*, 1861, **45** (2), 862.
7. Riesenfeld .. *Z. anorg. Chem.*, 1912, **74**, 48 and various papers in *Berichte* (1906-12).
8. Spitalsky .. *Ibid.*, 1907, **53**, 184 ; **54**, 184 ; **57**, 72 ; 1910, **69**, 169.

SPECTRAL AND COLLISION DATA OF CO^+ AND THE DISSOCIATION ENERGY OF CARBON MONOXIDE

BY R. K. ASUNDI

(College of Science, Benares Hindu University)

Received June 9, 1943

THAT the energy of dissociation of carbon monoxide, $D(\text{CO})$ cannot be much less than 10 e.v., was shown to be deducible from a number of considerations.¹ Recently, Gaydon and Penney have suggested that $D(\text{CO})$ lies between 9.85 and 11.11 e.v.² The spectrum of CO^+ corroborating the data on collision processes further offers some interesting evidence bearing on this subject.

The dissociation energy of CO is 2.9 or 0.55 e.v. more than that of CO^+ according as $D(\text{CO}^+) = D(\text{CO}) + I(\text{C}) - I(\text{CO})$ or $D(\text{CO}^+) = D(\text{CO}) + I(\text{O}) - I(\text{CO})$. The three known electronic states of CO^+ namely $X(^2\Sigma^+)$, $A(^2\Pi)$ and $B(^2\Sigma^+)$ give on linear extrapolation of the vibrational levels, energies of dissociation of 9.9, 6.0 and 3.7 e.v., and therefore dissociation limits of 9.9, 7.9 and 9.3 e.v., from the ground level of CO^+ respectively. The vibrational levels of these states are directly known upto energy values of 25,963 cm^{-1} or 3.22 e.v., 20,169 cm^{-1} or 2.5 e.v., and 14,543 cm^{-1} or 1.8 e.v., respectively.³ Thus the extrapolation of B state is of the same order of accuracy as that of the ground state of CO. The extrapolation of A is less accurate and that of X looks comparatively long. To avoid further complications in the correlation of dissociation products the latter is generally considerably discounted.

Biskamp has observed perturbations in $v=7$ level of B state.⁴ From calculations made by us these appear to be vibrational perturbations caused by the vibrational levels of X state. Counting from the ground state of CO^+ the energy of X at $v=33$ is 55,982 cm^{-1} or 6.9 e.v., and that of B in the seventh vibrational level is 56,330 cm^{-1} . If this interpretation is correct, we practically know the levels of X upto 6.9 e.v. Its extrapolation is then of at least an equal if not greater order of accuracy than of either A and B states of CO^+ or the ground state of CO.

If to the dissociation limits of X, A and B we add $I(\text{CO}) = 14.1$ e.v., we get 24, 22 and 23.4 e.v., respectively. These values can be correlated

to and should be regarded as being in agreement with those obtained by collision experiments,⁵ due regard being given to possible inaccuracies in both methods. Thus we identify the first two with 23.3 ± 0.2 and 20.9 ± 0.2 e.v. which are already attributed to the dissociation processes involving products $\text{C}(^3\text{P}) + \text{O}^+(^4\text{S})$ and $\text{C}^+(^2\text{P}) + \text{O}(^3\text{P})$ respectively. The third is identical with 22.8 ± 0.2 e.v., and represents the process in which a further excitation of O from ^3P to ^1D occurs in the second process. This is evident because the minimum spectroscopic value for the dissociation limit of B being already $1.8 + 5.64 = 7.44$ e.v., it is hardly possible to correlate it with that of the A state. It must therefore involve an excited O atom 1.93 e.v., ($^1\text{D} - ^3\text{P}$), above the limit of A. Also the limit of X should be 2.35 e.v., $\{\text{I}(\text{O}) - \text{I}(\text{C})\}$, above the limit of A. We thus conclude from spectral and collision data taken together that X is derived from $\text{C}(^3\text{P}) + \text{O}^+(^4\text{S})$, A from $\text{C}^+(^2\text{P}) + \text{O}(^3\text{P})$ and B from $\text{C}^+(^2\text{P}) + \text{O}(^1\text{D})$.

Such a possibility has been already indicated on other grounds.⁶ Atom or ion collision experiments are also interesting for this conclusion. The process $\text{CO}^+ \rightarrow \text{C}^+ + \text{O}$ is found to be particularly intense while $\text{CO}^+ \rightarrow \text{C} + \text{O}^+$ is weak and not certain.⁷ This is probably due to the circumstance that in such type of collisions, processes involving comparatively large changes in internuclear distances are likely to be more favoured. This distance r_e for X ($^1\Sigma$) of CO is 1.13 Å., while r_e values for X, A* and B states of CO^+ are 1.114, 1.195–1.209 and 1.168 Å., respectively. Thus in these experiments it is A ($^2\Pi$) which is directly reached by collision.

All these considerations show that only the extrapolation of state A is not very reliable. A glance at the values for this state deduced by various authors (namely 13.30 Herzberg,⁸ 14.07 Weizel, Jevons and Sponer: Reports) confirms this suspicion. We, therefore, believe that the dissociation limits for X, A and B states deducible from spectroscopic data are 9.9, 7.5 and 9.4 e.v., respectively. These yield for D(CO) the values 10.45 e.v., from X state and 10.4 e.v., from A state, values which are remarkably close. From collision data on similar interpretation, we obtain 9.2, 6.8 and 8.7 e.v., respectively yielding for D(CO) 9.75 e.v., from X and 9.7 e.v., from A. The mean of these four values is 10.1 e.v.

Anand has recently reported two Rydberg series in emission in the extreme short-wave spectrum of CO and deduces 14.5 e.v., as their common limit.⁹ If the interpretation is correct, the limit can only refer to the

* The values for the doublet state A quoted in the literature are evidently calculated on the wrong basis of regarding the (3, 0) comet-tail band as the (0, 0) band. The values quoted here are accordingly corrected.

X state of CO^+ , in which case the D (CO) spectroscopic value will have to be increased by 0.4 e.v.

REFERENCES

1. Asundi and Samuel, *Proc. Ind. Acad. Sci.*, 1936, **3**, 526.
2. Gaydon and Penney, *Nature*, 1942, **150**, 406.
3. Data from Sponer, except the excitation potential for A ($^2\Pi$) which is from Asundi, *Curr. Sci.*, 1940, **9**, 503.
4. Biskamp, *Zeit. f. Phys.*, 1933, **86**, 33.
5. Hagstrum and Tate, *P. R.*, 1941, **59**, 354.
6. Asundi and Samuel, *Proc. Ind. Acad. Sci.*, 1937, **5**, 235.
7. Friedlander and others, *Zeit. f. Phys.*, 1932, **76**, 62.
8. Herzberg, *ibid.*, 1929, **52**, 815.
9. Anand, *Sc. and Cult.*, 1942, **8**, 278.

SOME INTEGRALS INVOLVING HUMBERT FUNCTION

BY B. R. PASRICHA*

(Isabella Thoburn College, Lucknow)

Received September 26, 1942

(Communicated by Prof. B. S. Madhava Rao, D.Sc., F.A.Sc.)

1. HUMBERT† introduced in the year 1930 the function $J_{m,n}(x)$ defined by

$$J_{m,n}(x) = \frac{x^{m+n}}{3^{m+n} \Gamma(m+1) \Gamma(n+1)} {}_0F_2 \left(m+1, n+1; -\frac{x^3}{27} \right). \quad (1)$$

He has given‡ the following form for the operational image of this function

$$\frac{1}{p^{m-\frac{1}{2}n}} J_n \left(-2\sqrt{\frac{1}{p}} \right)^{\frac{2}{3}} \subset x^{\frac{2m-n}{3}} J_{m,n}(3\sqrt[3]{x}). \quad (2)$$

The object of this paper is to investigate, by the method of operational calculus, some integrals involving the product of two Humbert functions. ||

2. Putting $z = \left(-2\sqrt{\frac{1}{p}} \right)$ in the known result¶

$$\left(\frac{1}{2}z \right)^{k-m-n} J_m(az) J_n(bz) = \frac{a^m b^n}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r) \Gamma(k+r)}{r!} J_{k+2r}(z) \\ \times F_4(-r, k+r; m+1, n+1; a^2, b^2)$$

where F_4 denotes the Appell's function defined by

$$F_4(a, \beta; \gamma, \gamma'; x, y) = \sum_{m=0}^{\infty} \frac{(a, m) (\beta, m)}{(\gamma, m) (1, m)} F(a+m, \beta+m; \gamma'; y) x^m \quad (3)$$

* I am deeply indebted to Dr. R. S. Varma for suggesting this problem to me and for his guidance in the preparation of this paper.

† P. Humbert, "Les fontions de Bessel du triosieme ordre," *Atti Pont Acad. della Scienza*, (Sess III del 16 Febbraio, 1930), Anno 83, 128-46.

‡ P. Humbert, "Nouvelles remarques sur les fontions de Bessel du triosieme ordre," *ibid.*, (Sess IV del 18 Marxo, 1934), Anno 87, 323-31.

§ I have followed Dr. McLachlan in using the symbol \subset for the operational image of a function.

|| The name Humbert Functions as already adopted by Dr. R. S. Varma instead of Bessel Functions of the 3rd order has been preferred as the latter name is associated with functions of a different type.

¶ W. N. Bailey, *Quar. Journ. of Math.* (Oxford Series), 1935, 6, 235.

and then multiplying either side by $\frac{a^{2l-m} b^{2l'-n}}{p^{1+l+l'-\frac{1}{2}k}}$, we have

$$\begin{aligned} & \frac{1}{p} \cdot \frac{1}{\left(\frac{p}{a^2}\right)^{l-\frac{1}{2}m}} J_m \left(-2\sqrt{\frac{a^2}{p}}\right) \frac{1}{\left(\frac{p}{b^2}\right)^{l'-\frac{1}{2}n}} J_n \left(-2\sqrt{\frac{b^2}{p}}\right) \\ &= \frac{(-)^{m+n-k} a^{2l} b^{2l'}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r) \Gamma(k+r)}{r!} \\ & \quad \times \frac{1}{\frac{2(1+l+l'+r)-(k+2r)}{2}} J_{k+2r} \left(-2\sqrt{\frac{1}{p}}\right) \\ & \quad \times F_4(-r, k+r; m+1, n+1; a^2, b^2). \end{aligned} \quad (4)$$

Now we know* that if $\phi(p) \subset f(x)$

then $\phi(p/s) \subset f(sx) \quad s = \text{const.} > 0.$

Applying this to (2) we have

$$\frac{1}{\left(\frac{p}{a^2}\right)^{l-\frac{1}{2}m}} J_m \left(-2\sqrt{\frac{a^2}{p}}\right) \subset (a^2 x)^{\frac{2l-m}{3}} J_{l,m} (3\sqrt[3]{a^2 x})$$

and

$$\frac{1}{\left(\frac{p}{b^2}\right)^{l'-\frac{1}{2}n}} J_n \left(-2\sqrt{\frac{b^2}{p}}\right) \subset (b^2 x)^{\frac{2l'-n}{3}} J_{l',n} (3\sqrt[3]{b^2 x})$$

These together with the product theorem,* viz.,

if $\phi_1(p) \subset f_1(x)$ and $\phi_2(p) \subset f_2(x)$

then $\frac{1}{p} \phi_1(p) \phi_2(p) \subset \int_0^x f_1(t) f_2(x-t) dt$

give us the original of L.H.S. of (4) to be

$$\int_0^x (a^2 t)^{\frac{2l-m}{3}} [b^2 (x-t)]^{\frac{2l'-n}{3}} J_{l,m} (3\sqrt[3]{a^2 t}) J_{l',n} [3\sqrt[3]{b^2 (x-t)}] dt.$$

The original of R.H.S. of (4), obtained by term by term interpretation with the help of (2), is

$$\begin{aligned} & \frac{(-)^{m+n-k} a^{2l} b^{2l'} x^{\frac{2(1+l+l')-k}{3}}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r) \Gamma(k+r)}{r!} J_{1+l+l+r, k+2r} (3\sqrt[3]{x}) \\ & \quad \times F_4(-r, k+r; m+1, n+1; a^2, b^2) \end{aligned}$$

* Carson, *Electric Circuit Theory and Operational Calculus* (McGraw Hill, New York, 1936).

Hence Lerch's theorem gives that

$$\begin{aligned} & \int_0^x (a^2 t)^{\frac{2l-m}{3}} [b^2 (x-t)]^{\frac{2l-n}{3}} J_{l,m} (3\sqrt[3]{a^2 t}) J_{l',n} [3\sqrt[3]{b^2 (x-t)}] dt \\ &= \frac{(-)^{m+n-k} a^{2l} b^{2l'} x^{\frac{2(l+l')-k}{3}}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r) \Gamma(k+r)}{r!} J_{1+l+l'+r, k+2r} (3\sqrt[3]{x}) \\ & \quad \times F_4(-r, k+r; m+1, n+1; a^2, b^2). \end{aligned} \quad (5)$$

3. It is easy to see that the known relation*

$$\begin{aligned} (A) \left(\frac{1}{2} bz\right)^{m-n} J_n(bz) &= b^m \sum_{r=0}^{\infty} \frac{\Gamma(m+r)}{r! \Gamma(n+r)} F(m+r, -r; n+1; k^2) \\ & \quad \times (n+2r) J_{m+2r}(z) \end{aligned}$$

by the above method gives the result†

$$\begin{aligned} J_{l,n} (3\sqrt[3]{b^2 x}) &= (-)^{n-m} b^{\frac{2}{3}(l+n)} x^{\frac{1}{3}(n-m)} \sum_{r=0}^{\infty} \frac{\Gamma(m+r)}{r! \Gamma(n+1)} (n+2r) J_{l+r, m+2r} (3\sqrt[3]{x}) \\ & \quad \times F(m+r, -r; n+1; k^2) \end{aligned} \quad (6)$$

and that the known relation‡

$$\begin{aligned} (B) \left(\frac{1}{2} z\right)^{k-m-n} J_m(az) J_n(bz) &= \frac{a^m b^n \Gamma(k+1)}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(\frac{1}{2}z)^r}{r!} J_{k+r}(z) \\ & \quad \times F_4(-r, k+1; m+1, n+1; a^2, b^2) \end{aligned}$$

gives the result

$$\begin{aligned} & \int_0^x (a^2 t)^{\frac{2l-m}{3}} J_{l,m} (3\sqrt[3]{a^2 t}) [b^2 (x-t)]^{\frac{2l-n}{3}} J_{l',n} [3\sqrt[3]{b^2 (x-t)}] dt \\ &= \frac{(-)^{m+n-K} \Gamma(k+1) a^{2l} b^{2l'} x^{\frac{2(l+l')-K}{3}}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(-)^r x^{r/3}}{r!} J_{1+l+l'+r, k+r} (3\sqrt[3]{x}) \\ & \quad \times F_4(-r, k+1; m+1, n+1; a^2, b^2). \end{aligned} \quad (7)$$

4. As another illustration of the above method we, by putting

$$z = \left(-2 \sqrt{\frac{1}{p}}\right) \text{ in}$$

* Watson, *Bessel Functions* (Camb. Univ. Press, 1922), p. 140.

† This result has been included here because it gives the expansion of a Humbert function in an infinite series involving Humbert functions.

‡ Bailey, *loc. cit.*

$$J_m(z) J_n(z) = \frac{1}{\Gamma(m+1) \Gamma(n+1)} \left(\frac{z}{2}\right)^{m+n} {}_2F_3\left(\begin{matrix} \frac{1+m+n}{2}, \frac{2+m+n}{2}; \\ 1+m, 1+n, 1+m+n; \end{matrix} -z^2\right)^*$$

get that

$$\begin{aligned} & \frac{1}{p} \cdot \frac{1}{p^{\frac{2a-m}{2}}} J_m\left(-2\sqrt{\frac{1}{p}}\right) \cdot \frac{1}{p^{\frac{2a'-n}{2}}} J_n\left(-2\sqrt{\frac{1}{p}}\right) \\ &= \frac{(-)^{m+n}}{\Gamma(m+1) \Gamma(n+1) p^{1+a+a'}} {}_2F_3\left(\begin{matrix} \frac{1+m+n}{2}, \frac{2+m+n}{2}; \\ 1+m, 1+n, 1+m+n; \end{matrix} -\frac{4}{p}\right) \quad (8) \end{aligned}$$

The original of L.H.S. of this is evidently

$$\int_0^x t^{\frac{2a-m}{3}} (x-t)^{\frac{2a'-n}{3}} J_{a,m}(3\sqrt[3]{t}) J_{a',n}(3\sqrt[3]{x-t}) dt.$$

R.H.S. of (8)

$$\begin{aligned} & \frac{(-)^{m+n}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\left(\frac{1+m+n}{2}, r\right) \left(\frac{2+m+n}{2}, r\right)}{r! (1+m, r) (1+n, r) (1+m+n, r)} \times \frac{(-4)^r}{p^{1+a+a'+r}} \\ & \subset \frac{(-)^{m+n}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\left(\frac{1+m+n}{2}, r\right) \left(\frac{2+m+n}{2}, r\right)}{r! (1+m, r) (1+n, r) (1+m+n, r)} \times \frac{(-4)^r x^{1+a+a'+r}}{\Gamma(2+a+a'+r)} \\ &= \frac{(-)^{m+n} x^{1+a+a'}}{\Gamma(m+1) \Gamma(n+1) \Gamma(2+a+a')} {}_2F_4\left(\begin{matrix} \frac{1+m+n}{2}, \frac{2+m+n}{2}; \\ 1+m, 1+n, 1+m+n, 2+a+a'; \end{matrix} -4x\right). \end{aligned}$$

Hence

$$\begin{aligned} & \int_0^x t^{\frac{2a-m}{3}} (x-t)^{\frac{2a'-n}{3}} J_{a,m}(3\sqrt[3]{t}) J_{a',n}(3\sqrt[3]{x-t}) dt \\ &= \frac{(-)^{m+n} x^{1+a+a'}}{\Gamma(m+1) \Gamma(n+1) \Gamma(2+a+a')} {}_2F_4\left(\begin{matrix} \frac{1+m+n}{2}, \frac{2+m+n}{2}; \\ 1+m, 1+n, 1+m+n, 2+a+a'; \end{matrix} -4x\right) \end{aligned}$$

The following cases in which the function on the R.H.S. of the general result (9) reduces to Humbert function deserve special mention:

* Whittaker and Watson, *Modern Analysis* (4th Ed.), p. 380.

I. Taking $(1+m+n)/2 = 1+m$ and $(2+m+n)/2 = 1+m+n$, we have

$$\begin{aligned} \int_0^x t^{\frac{4a+1}{6}} (x-t)^{\frac{4a'-1}{6}} J_{a,-\frac{1}{2}}(3\sqrt[3]{t}) J_{a',\frac{1}{2}}(3\sqrt[3]{x-t}) dt \\ = \frac{x^{\frac{2}{3}(a+a')+\frac{1}{2}}}{\sqrt{\pi} 2^{\frac{2}{3}(a+a')+1}} J_{\frac{1}{2}, 1+a+a'}(3\sqrt[3]{4x}) \end{aligned} \quad (10)$$

II. Taking $(1+m+n)/2 = 1+m$ and $(2+m+n)/2 = 2+a+a'$, we get that

$$\begin{aligned} \int_0^x t^{\frac{2a-2a'-1}{6}} J_{a, a+a'+\frac{1}{2}}(3\sqrt[3]{t}) (x-t)^{\frac{2a'-2a-3}{6}} J_{a', a+a'+\frac{3}{2}}(3\sqrt[3]{x-t}) dt \\ = \frac{(-)^{2(a+a')}}{\sqrt{\pi} 2^{1/3} x^{1/6}} J_{a+a'+\frac{3}{2}, 2(1+a+a')}(3\sqrt[3]{4x}) \end{aligned} \quad (11)$$

III. If $(1+m+n)/2 = 1+m+n$ and $(2+m+n)/2 = 1+n$, then

$$\begin{aligned} \int_0^x t^{\frac{4a+1}{6}} (x-t)^{\frac{4a'+1}{6}} J_{a,-\frac{1}{2}}(3\sqrt[3]{t}) J_{a',-\frac{1}{2}}(3\sqrt[3]{x-t}) dt \\ = -\frac{x^{\frac{2}{3}(a+a')+\frac{5}{6}}}{\sqrt{\pi} 2^{\frac{2}{3}(a+a')+\frac{1}{2}}} J_{-\frac{1}{2}, 1+a+a'}(3\sqrt[3]{4x}) \end{aligned} \quad (12)$$

IV. Taking $(1+m+n)/2 = 2+a+a'$ and $(2+m+n)/2 = 1+n$, we have

$$\begin{aligned} \int_0^x t^{\frac{2a-2a'-3}{6}} J_{a, a+a'+3/2}(3\sqrt[3]{t}) (x-t)^{\frac{2a'-2a-3}{6}} J_{a', a+a'+3/2}(3\sqrt[3]{x-t}) dt \\ = \frac{(-)^{2a+2a'+1}}{\sqrt{\pi x}} J_{a+a'+\frac{3}{2}, 2a+2a'+3}(3\sqrt[3]{4x}) \end{aligned} \quad (13)$$

V. Two more cases are possible when $a+a'+(3/2)=0$.

(i) If $(1+m+n)/2 = 1+m+n$ and $(2+m+n)/2 = 2+a+a'$, we have

$$\begin{aligned} \int_0^x t^{\frac{2a-m}{3}} J_{a,m}(3\sqrt[3]{t}) (x-t)^{\frac{m-2a-2}{3}} J_{-a-3/2, -(1+m)}(3\sqrt[3]{x-t}) dt \\ = -\frac{2^{2/3}}{\sqrt{\pi} x^{1/6}} J_{m, -(1+m)}(3\sqrt[3]{4x}) \end{aligned} \quad (14)$$

(ii) Taking $(1+m+n)/2 = 2+a+a'$ and $(2+m+n)/2 = 1+m+n$,

we get

$$\int_0^x t^{\frac{2a-m}{3}} J_{a,m} (3\sqrt[3]{t}) (x-t)^{\frac{m-2a-3}{3}} J_{-a-3/2,-m} (3\sqrt[3]{x-t}) dt$$

$$= \frac{1}{\sqrt{\pi x}} J_{m,-m} (3\sqrt[3]{4x}), \quad (15)$$

provided that in these two results m is not an integer.

5. When the above method with the substitution $z = \frac{1}{p^2}$ is applied to

$${}_1F_1(a; \rho; z) \times {}_1F_1(a; \rho; -z) = {}_2F_3(a, \rho-a; \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}; \frac{1}{4}z^2)^*$$

we get the result

$$\int_0^x {}_1F_3\left(a; \rho, \frac{1}{2}, 1; \frac{t^2}{4}\right) \times {}_1F_3\left(a; \rho, \frac{1}{2}, 1; -\left(\frac{x-t}{2}\right)^2\right) dt$$

$$= x {}_2F_7\left(a, \rho-a; \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \frac{x^4}{1024}\right) \quad (16)$$

We shall here also note three special cases—

(i) If $a = \rho$,

$$\int_0^x [-t^2(x-t)^2]^{1/6} J_{-\frac{1}{2},0} \left(3\sqrt[3]{-\frac{t^2}{4}}\right) \times J_{-\frac{1}{2},0} \left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt = \frac{x^{2^{2/3}}}{\pi} \quad (17)$$

(ii) when $a = 1/2$,

$$\int_0^x [-t^2(x-t)^2]^{\frac{1-\rho}{3}} J_{-1+\rho,0} \left[3\sqrt[3]{-\frac{t^2}{4}}\right] \times J_{-1+\rho,0} \left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt$$

$$= \frac{x}{(\Gamma\rho)^2 2^{\frac{4}{3}(\rho-1)}} {}_1F_6\left(\rho - \frac{1}{2}; \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \frac{x^4}{1024}\right) \quad (18)$$

(iii) taking $a = 1$ we have

$$\int_0^x [-t^2(x-t)^2]^{\frac{1}{2}-\rho/3} J_{\rho-1,-\frac{1}{2}} \left(3\sqrt[3]{-\frac{t^2}{4}}\right) J_{\rho-1,-\frac{1}{2}} \left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt$$

$$= \frac{4x}{\{\Gamma(\rho)\}^2 \pi 2^{\frac{4}{3}\rho}} {}_1F_6\left(\rho - 1; \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}, \frac{3}{4}, \frac{5}{4}; \frac{x^4}{1024}\right) \quad (19)$$

* Bailey, "Products of generalised hypergeometric series," *Proc. Lond. Math. Soc.*, 1928, (2), 28, 242-54.

6. The same operator $z = \frac{1}{p^2}$ when applied to the known result*

$$\begin{aligned} & {}_1F_1(a; \rho; x) \times {}_1F_1(a - \rho + 1; 2 - \rho; -x) \\ &= {}_2F_3\left(\begin{matrix} a - \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}\rho - a + \frac{1}{2}; \\ \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}, \frac{3}{2} - \frac{1}{2}\rho; \end{matrix} \frac{1}{4}x^2\right) + \frac{(2a - \rho)(1 - \rho)x}{\rho(2 - \rho)} \\ &\times {}_2F_3\left(\begin{matrix} a - \frac{1}{2}\rho + 1, \frac{1}{2}\rho - a + 1; \\ \frac{1}{2}\rho + 1, \frac{3}{2}, 2 - \frac{1}{2}\rho; \end{matrix} \frac{1}{4}x^2\right) \end{aligned}$$

gives the result

$$\begin{aligned} & \int_0^x {}_1F_3\left(\begin{matrix} a; \\ \rho, \frac{1}{2}, 1; \end{matrix} \frac{t^2}{4}\right) \times {}_1F_3\left[\begin{matrix} a - \rho + 1; \\ 2 - \rho, \frac{1}{2}, 1; \end{matrix} -\left(\frac{x-t}{2}\right)^2\right] dt \\ &= x {}_2F_7\left(\begin{matrix} a - \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}\rho - a + \frac{1}{2}; \\ \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}, \frac{3}{2} - \frac{1}{2}\rho, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \end{matrix} \frac{x^4}{1024}\right) + \frac{(2a - \rho)(1 - \rho)x^3}{6\rho(2 - \rho)} \\ &\times {}_2F_7\left(\begin{matrix} a - \frac{1}{2}\rho + 1, \frac{1}{2}\rho - a + 1; \\ \frac{1}{2}\rho + 1, \frac{3}{2}, 2 - \frac{1}{2}\rho, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \end{matrix} \frac{x^4}{1024}\right) \end{aligned} \quad (20)$$

As in § 5 four particular cases deserve attention:

I. (i) $\alpha = \rho$,

$$\begin{aligned} & \int_0^x (-t^2)^{\frac{1}{6}} (x-t)^{\frac{2\rho-1}{3}} J_{-\frac{1}{2}, 0}\left(3\sqrt{\frac{-t^2}{4}}\right) J_{1-\rho, -\frac{1}{2}}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt \\ &= \frac{2^{\frac{2\rho}{3}} x}{\Gamma(2 - \rho) \pi} {}_1F_6\left(\begin{matrix} -\frac{1}{2}\rho + \frac{1}{2}; \\ \frac{1}{2}, \frac{3}{2} - \frac{1}{2}\rho, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \end{matrix} \frac{x^4}{1024}\right) + \frac{2^{\frac{2\rho-3}{3}} x^3 (1 - \rho)}{3\pi \Gamma(3 - \rho)} \\ &\times {}_1F_6\left(\begin{matrix} -\frac{1}{2}\rho + 1; \\ \frac{3}{2}, 2 - \frac{1}{2}\rho, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \end{matrix} \frac{x^4}{1024}\right) \end{aligned} \quad (21)$$

(ii) If $\alpha = 1$,

$$\begin{aligned} & \int_0^x (-t^2)^{\frac{1}{2}-\frac{1}{3}\rho} (x-t)^{\frac{1}{3}} J_{\rho-1, -\frac{1}{2}}\left(3\sqrt{\frac{-t^2}{4}}\right) J_{-\frac{1}{2}, 0}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt \\ &= \frac{x}{\pi \Gamma(\rho) 2^{\frac{2\rho-4}{3}}} {}_1F_6\left(\begin{matrix} -\frac{1}{2} + \frac{1}{2}\rho; \\ \frac{1}{2}\rho + \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \end{matrix} \frac{x^4}{1024}\right) \\ &+ \frac{x^3 (1 - \rho)}{3\pi \Gamma(1 + \rho) 2^{\frac{2\rho-4}{3}}} {}_1F_6\left(\begin{matrix} \frac{1}{2}\rho; \\ \frac{1}{2}\rho + 1, \frac{3}{2}, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \end{matrix} \frac{x^4}{1024}\right) \end{aligned} \quad (22)$$

* Bailey, *ibid.*

II. (i) If $a = 1/2$,

$$\begin{aligned} & \int_0^1 (-t^2)^{\frac{1}{2}(1-\rho)} J_{\rho-1,0} \left(3 \sqrt{\frac{-t^2}{4}} \right) \times {}_1F_3 \left[\begin{matrix} \frac{3}{2}-\rho \\ 2-\rho, \frac{1}{2}, 1 \end{matrix}; -\left(\frac{x-t}{2}\right)^2 \right] dt \\ &= \frac{x}{\Gamma(\rho)} 2^{\frac{3}{2}(\rho-1)} {}_2F_7 \left(\begin{matrix} 1-\frac{1}{2}\rho, \frac{1}{2}\rho; \\ \frac{1}{2}\rho+\frac{1}{2}, \frac{1}{2}, \frac{3}{2}-\frac{1}{2}\rho, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \end{matrix} \frac{x^4}{1024} \right) \\ &+ \frac{x^3(1-\rho)^2}{3\Gamma(1+\rho)(2-\rho)2^{\frac{3}{2}\rho+\frac{1}{2}}} {}_2F_7 \left(\begin{matrix} \frac{3}{2}-\frac{\rho}{2}, \frac{1}{2}\rho+\frac{1}{2}; \\ \frac{1}{2}\rho+1, \frac{3}{2}, 2-\frac{1}{2}\rho, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \end{matrix} \frac{x^4}{1024} \right) \end{aligned} \quad (23)$$

(ii) If $a = \rho - \frac{1}{2}$,

$$\begin{aligned} & \int_0^1 {}_1F_3 \left(\begin{matrix} \rho-\frac{1}{2}; \\ \rho, \frac{1}{2}, 1 \end{matrix}; \frac{t^4}{4} \right) (x-t)^{\frac{3}{2}\rho-\frac{3}{2}} J_{1-\rho,0} \left[3 \left(\frac{x-t}{2} \right)^{2/3} \right] dt \\ &= \frac{x 2^{\frac{3}{2}\rho-\frac{3}{2}}}{\Gamma(2-\rho)} {}_2F_7 \left(\begin{matrix} \frac{1}{2}\rho; 1-\frac{1}{2}\rho \\ \frac{1}{2}\rho+\frac{1}{2}, \frac{1}{2}, \frac{3}{2}-\frac{1}{2}\rho, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}; \end{matrix} \frac{x^4}{1024} \right) - \frac{x^3(1-\rho)^2}{3\rho \Gamma(3-\rho)} \\ &\times \frac{1}{2^{\frac{5}{2}-\frac{1}{2}\rho}} {}_2F_7 \left(\begin{matrix} \frac{1}{2}\rho+\frac{1}{2}, \frac{3}{2}-\frac{1}{2}\rho; \\ \frac{1}{2}\rho+1, \frac{3}{2}, 2-\frac{1}{2}\rho, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}; \end{matrix} \frac{x^4}{1024} \right). \end{aligned} \quad (24)$$

7. It remains to discuss the convergence of the infinite series occurring in results (5)–(7).

Taking the result (5) we have the general term* of F_4 to be less than

$$\sum_{\mu=0}^{\infty} \mu^{2s+k-2} (a+b)^{2\mu}, \quad s \text{ is +ive and } > -m \text{ and } -n.$$

Further

$$J_{1+l+l'+r, k+2r} (3 \sqrt[3]{x}) = \left[\frac{x^{r+\frac{1}{2}(1+l+l'+k)}}{\Gamma(2+l+l'+r) \Gamma(1+k+2r)} \right] \times [1 + O(r^{-2})]$$

Using this and the Stirling's formula

$$\Gamma(x) = x^{x-\frac{1}{2}} e^{-x} (2\pi)^{\frac{1}{2}} e^{\theta/(12x)}, \quad 0 < \theta < 1$$

we† have

$$\begin{aligned} & \frac{\Gamma(k+2r) \Gamma(k+r)}{r!} x^{\frac{3}{2}(1+l+l')-\frac{1}{2}k} J_{1+l+l'+r, k+2r} (3 \sqrt[3]{x}) \\ &= O \left[\frac{(xe)^r}{r^{r+l+l'-k+7/2}} \right] \end{aligned}$$

* W. N. Bailey, "Generalized Hypergeometric Series" (*Cambridge Tracts in Mathematics and Mathematical Physics*, No. 32, 1935), p. 75.

† Dr. R. S. Varma, "On Humbert Functions," *Annals of Math.*, 1941, 42, 429-36.

These give that the series on the right of (5) is less than

$$(-)^{m+n-K} \frac{a^{2l} b^{2l'} x^{1+l+l'}}{\Gamma(m+1) \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(xe)^r}{r^{r+l+l'-K+7/2}} \sum_{\mu=0}^{\infty} \mu^{2s+K-2} (a+b)^{2\mu}$$

which is convergent when $(a+b) < 1$.

Hence the infinite series on the right of (5) is convergent under the condition stated just above.

The series on the right of (7) also converges under the same condition.

Further it is easy to see that the general term of the series on the right of (6)

$$= O \left[\frac{(-x k^2 e^2)^r}{r^{2r+l+n+1}} \right]$$

and accordingly the series is convergent.

DYNAMICS OF THUNDERSTORMS*

BY S. L. MALURKAR

Received 5, 1943

THUNDERSTORMS are of such frequent occurrence and are of such great importance in meteorology, that every attempt at clarification of the processes involved would have a sufficient justification. It is but natural that the thermodynamic aspect has taken the major portion of the discussions on the subject, as energy in the form of heat plays a large role in the phenomenon. The dynamical aspect of the convective currents is also vital to the production of the thunderstorm and an enquiry into it is called for.

The preliminary background was obtained by an examination of the actual upper air soundings made at Poona. The occasions when successful soundings have been made during thunderstorms at a given place are small and the number of observations during the successive development of a thunderstorm still less. The limitation set by the number of observations at a place on days of thunderstorms can be overcome by assuming that the meteorological conditions existing at stations in the neighbourhood of places recording thunderstorms give a fairly good picture of conditions before the onset of thunderstorms. The analysis yielded the following ideas:—

(a) In general, the potential temperature of air increased with height, *i.e.*, the lapse rate was less than dry adiabatic. But on certain days, the rise of potential temperature with height was less marked and in some cases there was no appreciable rise for a thickness of one or two kilometres, *i.e.*, the lapse rate was or very nearly was dry adiabatic. On the days when the lapse rate was nearly dry adiabatic, there was a tendency for thunderstorms to occur in the neighbourhood of Poona.

(b) However, when the lapse rate was nearly adiabatic and the humidity of air small the distribution of thunderstorms was poor or absent.

(c) The air was not necessarily saturated in the lower layers of the atmosphere on days of thunderstorms.

The development of a thunderstorm which is essentially a convective phenomenon needs *a cause for initial convection and then a possibility of its maintenance once the convection has been started.*

* Substance of a colloquium given at the Meteorological Office, Poona, in March 1934.

There has been considerable discussion in meteorological literature regarding the existence of potentially colder air superposed over potentially warmer air. If this superposition existed, it may be argued that the system being unstable, may initiate convection and even possibly maintain it. It is theoretically conceivable to have small isolated masses of air which may be potentially colder than the air below it. But it is not evident, whether it is ever possible to have a potentially colder stratum of air superposed over a potentially warmer one for any considerable area or over a long period. Further if such a superposition has once existed for some time, due to certain boundary conditions, it may not give rise to upward motion by itself. A slight digression on this point may not be out of place.

Rayleigh¹ showed as a result of Bernard's experiments, that in shallow layer of liquid the temperature of the lower surface could be increased above the temperature of the top surface upto a certain limit before instability set in. Brunt and Low tried to apply this result to the existence of large lapse rates near the ground on hot days. Later Jeffreys improved on Rayleigh's results and obtained similar expressions for instability, but he "could not say how far the result could apply to the atmosphere". Hales, applying the theory to the atmosphere, showed that the *form* of the result was not different from that obtained by the previous workers and deduced that only over a limited height, super-adiabatic lapse rates may occur, *i.e.*, the potential temperature cannot decrease with height for any large interval of height.

It may be argued that the top-heaviness due to the difference in the moisture content in different layers may lead to a different form of result and bring about instability. This can be disposed of without great details. The fundamental equations of instability in the thermal problem for a thin layer of air are:

$$d/dt (u, v, w) - \nu \rho \Delta (u, v, w) = - (\partial/\partial x, \partial/\partial y, \partial/\partial z) \cdot p - (o, o, g\rho) \quad (1)$$

$$d\rho/dt = \rho \operatorname{div}. (u, v, w) \quad (2)$$

$$d\theta/dt = k \Delta \theta \quad (3)$$

$$\rho = \rho_0 (1 - \alpha\theta), \quad (4)$$

¹ Rayleigh, *Phil. Mag.*, 32, 529. *Coll. Works*, 6, 432. Low, *Nature*, 65, 299. Brunt, *ibid.*, 300. Jeffreys, *Phil. Mag.*, 1926, 2, 833 and *Proc. Roy. Soc.*, 1928, 118, 195. Low, *Proc. Roy. Soc.*, 1929, 125, 180. Jeffreys, *Proc. Camb. Phil. Soc.*, 1931, 26, 170. Malurkar, *Gerland's Beitr. Geophys.*, 1937, 51, 270. Hales, *Proc. Roy. Soc.*, 151, 624. Also Malurkar in the Abstracts Nos. 28, 29, 37 of 1937 of the Physics Section of the Indian Science Congress.

where u, v, w are components or velocity of the fluid, p is the pressure, ρ the density at any point, ν the viscosity, θ the temperature, k the thermal diffusivity, ρ_0 the initial density and α is a constant. The z -axis is measured vertically upwards and Δ is used as usual for $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

The equations (1) and (2) do not explicitly involve temperature; (1) is the general equation of motion in a fluid taking account of viscosity and (2) is the equation of continuity. But equations (3) and (4) depend on temperature. Taylor² showed that in eddy diffusion, the moisture content or more accurately the mixing ratio obeyed an equation similar to the equation of heat conductivity. It is also well known that the density of air and the mixing ratio have a linear relation when thin layers are considered. If a thin layer of uniform temperature is considered and r the mixing ratio is taken to decrease uniformly with height to bring about top-heaviness equations (3) and (4) are replaced by similar equations involving mixing ratio

$$dr/dt = k' \Delta r \quad (5)$$

$$\rho = \rho_0 (1 - \alpha' r). \quad (6)$$

The limits of instability can be worked out exactly as in the thermal problem except that the term mixing ratio replaces temperature at each stage of calculation.

The criterion of instability would be, in terms of density, $(\rho_1 - \rho_0)/\rho_0 < K k \nu / g h^3$, where ρ_1 is the density of the top-layer, h the thickness of the layer and K is a constant depending on the boundary conditions. Though investigation on the analogy of Hales to the whole atmosphere, with moisture as variable, has not been carried out, the nature of the equations allow one to be confident that that the criteria of instability brought about by top-heaviness due to temperature gradient and that due to the gradient of mixing ratio are at least to a first approximation analogous.

It follows that between narrow limits, it may be possible to have top-heaviness owing to higher potential temperature at the lower levels or owing to injection of extra moisture in the lower layers. But instability rapidly sets in if the height interval is large. The top-heaviness which can exist in very shallow layers as deduced in the various papers on the basis of stability would not allow instability to set in without external stimulus; or initiation of convection without external stimulus is not likely in such systems. The cause of initial upward motion must, therefore, be sought for elsewhere

² Taylor, *Phil. Trans. Roy. Soc.*, 1915, 215, 1.

than in the general or widespread temperature and humidity distribution that already exists. The possible local causes of upward motion are:

(a) Strong *unequal* surface heating—If there was equal heating of the various strata in the very low layers of the atmosphere, the criteria developed previously may perhaps give rise to large lapse rates without creation of instability when thin layers are considered. But when there is unequal heating in any level such isolated stable strata or pockets of air do not form and upward motion is facilitated. In nature, the unequal heating is more likely; due to the fact that large tracts are covered by vegetation and others bare. The rivers, large water surfaces, uneven land or land not covered uniformly by vegetation or even non-uniform distribution of rocks and earth make the surfaces of equal temperature deviate largely from a horizontal position and upward motion can be initiated. The deviation of the isothermal surfaces from the horizontal would generally be great during the afternoons and early evenings. Even at other times, the non-horizontality of the isothermal surfaces brought about by differential cooling of the land and water surfaces may give rise to upward currents. When the top surface of a cloud cools by radiation and sinks, upward motion may indirectly be induced.

(b) If the surfaces of equal humidity are not horizontal and the gradient of humidity or mixing ratio sufficient, upward currents can be initiated. The analogy with temperature gradient can profitably be used.

(c) At the surface of separation of two air masses large waves may be set up and in portions of the wave, upward motion is possible.

(d) Gradient of wind velocity due either to (i) orography, or (ii) juxtaposition of two air masses with very different horizontal velocities. When land rises abruptly, there is an upward component of wind whenever the wind blows against the land. When two air masses meet with very different horizontal velocities the equation of continuity would indicate that large upward motion of air can take place. At a cold front or whenever there is wedge of cold air, the air adjacent to it will be lifted up.

In the large-scale operations of the atmosphere, a mass of air rising due to unequal heating may be considered as an isolated air mass obeying the well-known equation

$$\frac{d^2z}{dt^2} = g (\theta_r/\theta_a - 1), \quad (1)$$

where θ_r is the temperature of the rising mass, θ_a is the temperature of the air immediately surrounding it and z is the vertical height measured upwards. The friction and the dissipative forces have been neglected. The

equation cannot be solved in general. A simple case of an atmosphere with a uniform lapse rate μ can be taken. At the initial level the temperature of the free air may be θ and that of the rising air $\theta + \alpha$. The rising air cools at the dry adiabatic rate λ . At the initial level the rising mass may be taken to have no upward extra velocity imparted to it, *i.e.*, would start from rest. Then

$$\frac{d^2z}{dt^2} = g(a - \lambda z + \mu z)/(\theta - \mu z) \quad (8)$$

$$\frac{1}{2} \left(\frac{dz}{dt} \right)^2 = g/\mu^2 \{ (\lambda - \mu) \mu z - (\alpha\mu - \lambda\theta + \mu\theta) \log(1 - \mu z/\theta) \} \quad (9)$$

dz/dt would be zero at $z=0$ and again at the point given by

$$\mu(\lambda - \mu)z = (\alpha\mu - \lambda\theta + \mu\theta) \log(1 - \mu z/\theta). \quad (10)$$

As θ is large compared with λ , μ or z the equation can be approximately solved and dz/dt is equal to zero at

$$2\alpha \left/ \left(\lambda - \mu - \frac{\alpha\mu}{\theta} \right) \right. \quad (11)$$

while $d^2z/dt^2 = 0$ at $\alpha/(\lambda - \mu)$.

The level to which a mass of air rises due to its being lighter than its surroundings at any stage is not limited by the fact that at the terminal position the density must be equal to that of the surrounding air. The acceleration alone is reduced to nothing at the point of hydrostatic equilibrium. The momentum developed by the rising current would be able to carry the mass to a level considerably above the level of hydrostatic equilibrium. When this rising mass, after having overshoot the hydrostatic equilibrium level, comes to rest at the hydrodynamic equilibrium level, it would be colder or denser than its immediate surroundings and would descend. Similarly during descent, the mass would go quite well below the level of hydrostatic equilibrium and find itself warmer or lighter than its surroundings. It will rise again and would execute oscillations. The initial amplitude would be small if the rise of potential temperature with height was large as the rising mass has nearly a constant potential temperature. If the increase in potential temperature with height is relatively smaller the amplitude of the oscillations would correspondingly be greater.

In any particular problem, however, the successive amplitudes diminish, perhaps rapidly, due to the dissipative forces like resistance and mixing. For the problem on hand, it is not necessary that oscillations *should take place* but that the rising mass must be able to go above the level of static equilibrium.

In the thermodynamic treatment, the actual mode of rise of air is not very material. And often, the treatment is more or less static. The importance of the extra ascent between the levels of static and dynamic equilibrium is that though a mass of unsaturated air may not reach the stage of condensation before the static level, yet it may attain saturation before the dynamic level of equilibrium is reached. In the above equations it is easily seen that the extra height between the levels of static and dynamic levels is nearly of the same order as that between the initial level and the level of static equilibrium. In other words a mass of air which would have cooled by 10°C . by rising one kilometre to reach its static level of equilibrium may cool nearly 15 to 20°C . before the dynamic level of equilibrium is reached. The difference involved is obvious. The dynamical treatment allows the condensation point to be attained for a rising mass which is much drier than the semi-static treatment. If the condensation is reached before the level of static equilibrium is reached, no special complications arise.

When the rising mass attains its saturation point and condenses, latent heat, which is comparatively large for water vapour, is liberated and it heats the air immediately surrounding the rising mass. This heated air has the impetus to rise due to this extra energy and may in turn initiate further upward motion. The system becomes self-regenerating and, if conditions are favourable, may grow at a continuously accelerated pace to result in a thunderstorm.

If the initial upward movement is due to unequal distribution of humidity and there is sufficient gradient of humidity upwards, arguments similar to the ones above can be used by replacing lighter for warmer and denser for colder. Once the condensation point is reached and the latent heat warmed the surrounding air, the further development would be similar to the upward motion due to extra heat imparted to the rising mass.

When the upward movement is due to horizontal gradient of wind, either due to orography or frontal action, the density of air at the initial place of vertical motion is not lighter than the surrounding air. Hence the upward motion of air due to gradient of wind may be considered as analogous to the stage described in the previous paragraphs when the lighter air had passed the level of static equilibrium but not yet come to rest, *i.e.*, still possessed upward momentum. If this air reached its condensation point before the level of momentary rest is reached, the liberated latent heat would give the surrounding air impetus for further vertical motion after which the previous arguments may be applied.

In nature the conditions described as of distinct types do not occur individually. More than one condition is operative. The orography may be helped by extra surface heating and bringing in of moisture in the lower levels or relative drying up of higher levels.

Incidentally, it may be mentioned that during the process of condensation and vertical movement, strong horizontal winds would drift away the products of condensation and may inhibit the development of a thunderstorm. Weaker winds at higher levels would help the growth of a thunderstorm. The inversions may also help to conserve or localise the accumulation of energy. Every small addition of heat or moisture in the lower layers can be dissipated away by convection currents. The inversion by preventing these small currents would allow sufficient energy to be accumulated in the lower layers and when the convection is brought into play to counteract the effect of inversion, it may do so with explosive violence.

When a uniform plate is heated from below the convection currents that are set up form isolated upward streams. There is no general upward transference of air over the whole plate. The actual places where these small rising currents are set up probably depend on irregularities on the surface. Even otherwise the points of ascent would perhaps be determined by the physical characteristics of the plate, *e.g.*, the points of ascent would somewhat be similar to the nodes of the Chladni's figures on the plate. The problem in nature, the places of occurrence of heat thunderstorms, may be compared to the patterns of nodes and anti-nodes in a loaded plate with suitable boundary conditions corresponding to the rivers, hills and other items of orography. This analogy was thought out during a conversation with L. P. Cohen and may profitably be followed up.

From a practical point of view, the above discussion leads one to the useful conclusion in the case of heat thunderstorms: if at higher levels fresh air which is relatively cooler or potentially cooler than the one existed before or if at lower layers relatively warmer or potentially warmer and more moist air than that which existed earlier is brought about, the conditions become favourable for thunderstorms. If the convective currents are started these conditions would help to maintain convection and may give rise to thunderstorms.

Summary

The development of a thunderstorm which is essentially a convective phenomenon needs a cause for initial convection and then conditions for its maintenance once started. The possibility of the inherent instability due to potentially colder air superposed on potentially warmer air or the

analogous case of extra injection of moisture in the lower layers is shown to be not applicable in nature and that causes for initial convection must be found elsewhere than in the potential density distribution. Some of the causes are non-horizontality of surfaces of equal temperature and equal humidity; and gradient of wind velocity. It is shown that upward rise of air produced by unequal heating of the ground, does not stop where the rising mass of air attains a density equal to that of the environment (hydrostatic equilibrium), but continues to rise higher till the momentum developed is reduced to zero. The extent of over-shooting is nearly of the same order as the height between the initial level and the level of hydrostatic equilibrium. Once the condensation level is reached, it is well known that the convection will become regenerative due to the evolution of the latent heat of condensation. In the usual treatment of the problem, the ascending parcel of air is expected to condense at or before it reaches the level of hydrostatic equilibrium if it is to develop into a thunderstorm. The dynamical treatment outlined in this paper takes into consideration the overshooting of the parcel of air and thereby allows much drier air to reach condensation and thereafter maintain convection: and can thus account for a larger number of thunderstorms.

THE ACTION OF GRIGNARD REAGENTS ON BENZOPYRONES

Part I. Preparation of Some Chromenes from 4-Substituted Coumarins

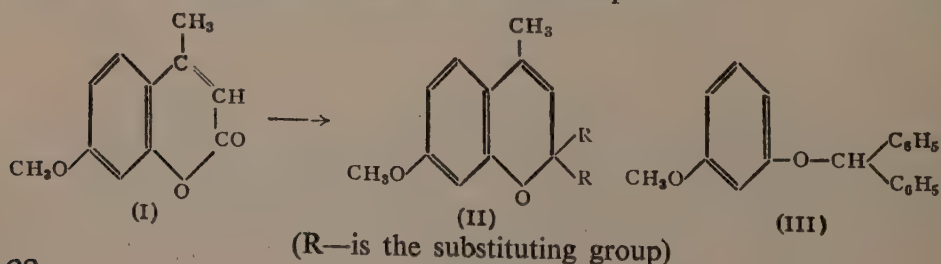
BY A. R. SUKUMARAN KARTHA AND K. N. MENON

(Maharaja's College, Ernakulam)

Received February 17, 1943

THE present investigation was undertaken with the object of synthesising compounds expected to possess insecticidal action similar to that of deguelin. With this object in view the action of grignard reagents on coumarins was taken up. This reaction was employed by Willstätter and co-workers¹ for the synthesis of anthocyanidines. Houben,² and Lowenbein, Pongracz and Spiess³ have also recorded a large number of investigations leading to the formation of substituted chromens and suggested a mechanism for the course of the reaction employing a large excess of the grignard reagent. Heilbron and Hill⁴ investigated the action of grignard reagents on substituted coumarins with the object of synthesising flavylum chlorides containing methoxyl and hydroxyl in the 4-position; the latter being expected readily to lose hydrogen chloride and pass into flavones. They obtained only diaryl products and consequently a detailed investigation of coumarins substituted in 3- and 4-positions was initiated. These investigations led them to the definite conclusion that the course of the reaction resulting in the production of either a Δ^2 or Δ^3 chromen is influenced solely by the position of the substituent in the pyran ring.

In this communication we are reporting the condensation of methoxymethyl umbelliferone with excess of grignard reagents prepared from (a) bromobenzene, (b) *p*-brom anisol, (c) benzyl chloride, (d) α -naphthyl bromide, and (e) methyl iodide. α -Naphthocoumarin was condensed with magnesium phenyl bromide. All these condensation products are assigned the Δ^3 -chromen structure in conformity with the general conclusions arrived at by Heilbron and co-workers, that namely when the 4-position is occupied by a substituent the product formed is the Δ^3 -compound.



The 2:2-diphenyl-4-methyl-7-methoxy- Δ^3 -chromen was subjected to alkaline hydrolysis yielding the diphenyl-methyl-ether (III) thereby confirming the Δ^3 -structure.

Experimental

The general methods of reaction and processing were the same in all cases and so the details are given only in one case.

2:2-Diphenyl-4-methyl-7-methoxy- Δ^3 -chromen.—The grignard reagent prepared from 3 grams (excess) of magnesium and the equivalent amount of bromobenzene was cooled in an ice-bath and treated with 5 grams of methoxy methyl umbelliferon in dry benzene. The reaction mixture was refluxed on the water-bath for 12 hours, decomposed with iced dilute hydrochloric acid and thoroughly extracted with benzene. After removing the benzene the residue was steamed to remove volatile impurities. The residue was extracted with ether, dried and solvent removed, yielding a solid melting at 60–65°. Repeated crystallisation from 95% alcohol yielded clusters of stout flat needles melting at 93°.

(Found: C, 84.1 and H, 6.6. $C_{23}H_{20}O_2$ requires 84.1 and 6.1 respectively.)

2:2-Dianisyl-4-methyl-7-methoxy- Δ^3 -chromen.—The crude product obtained from the reaction was a reddish viscous mass and on repeated crystallisation from absolute alcohol yielded needle-like tufts melting at 110°.

(Found: C, 77.4 and H, 6.2. $C_{25}H_{24}O_4$ requires 77.3 and 6.2 respectively.)

2:2-Dibenzyl-4-methyl-7-methoxy- Δ^3 -chromen.—The product of the reaction had first of all to be pressed on to a plate to remove the persistently adhering oily impurity and then crystallised from alcohol in rosettes of colourless needles melting at 52°.

(Found: C, 84.2 and H, 6.8. $C_{25}H_{24}O_2$ requires 84.3 and 6.7 respectively.)

2:2-Di- α -Naphthyl-4-methyl-7-methoxy- Δ^3 -chromen.—The viscous semisolid reaction mass was refluxed with excess of alcohol when an impurity was dissolved out and the product solidified. This processing was repeated with fresh alcohol each time till a fine colourless powder was obtained. Final crystallisation from glacial acetic acid gave a pure product melting at 240–41°.

(Found: C, 86.7 and H, 5.7. $C_{31}H_{24}O_2$ requires 86.9 and 5.6 respectively.)

2:2:4-Trimethyl-7-methoxy- Δ^3 -chromen.—The product is a liquid boiling at 158–60°/12 mm.

(Found: C, 76.1 and H, 7.9. $C_{13}H_{16}O_2$ requires 76.5 and 7.8 respectively.)

2:2-Diphenyl-4-methyl- α -naphtho- Δ^3 -chromen.—The product on crystallisation from a large volume of 95% alcohol yielded yellow prisms melting at 126–27°.

(Found: C, 89.5 and H, 6.3. $C_{26}H_{20}O_2$ requires 89.7 and 5.8 respectively.)

Alkaline hydrolysis of 2:2-Diphenyl-4-methyl-7-methoxy- Δ^3 -chromen.—2 Grams of the substance was refluxed with 50 c.c. of 50% potassium hydroxide for 60 hours. The solid melted and remained as a viscous liquid on the top of this alkaline solution. After hydrolysis was over the reaction mixture was diluted with 200 c.c. of water, cooled and extracted with ether. The ethereal extracts were united, dried over anhydrous magnesium sulphate and the ether removed. The residue weighed 1.2 grams and solidified to a hard mass. Crystallisation from alcohol yielded needles melting at 105.5°.

(Found: C, 82.3 and H, 6.1. $C_{20}H_{18}O_2$ requires 82.7 and 6.2 respectively.)

Summary

The action of grignard reagents on methoxy methyl umbelliferone and α -naphtho coumarin was investigated to prepare compounds similar to certain naturally occurring benzopyrans.

REFERENCES

1. *Ber.*, 1924, **57**, 1938, 1945.
2. *Ibid.*, 1904, **37**, 489.
3. *Ibid.*, 1924, **57**, 1517.
4. *J. C. S.*, 1927, 2005.

OPACITY CHANGES IN GEL-FORMING MIXTURES DURING SETTING

Part II. Thorium Phosphate, Cerium Phosphate, Thorium Arsenate and Stannic Phosphate Gels

BY T. V. DESAI AND S. GURUSWAMY

(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received May 24, 1943

(Communicated by Dr. Mata Prasad, D.Sc., F.I.C., F.A.Sc.)

In a previous communication Prasad and Gogate¹ have reported the results of the measurement of the opacity changes during the formation of thorium molybdate, stannic arsenate, and silicic acid gels with the help of a newly devised apparatus which involves the use of a compensated photocell circuit. The description of the apparatus is given in the author's paper (*loc. cit.*).

In the present investigation the study of the opacity changes has been continued by the same apparatus during the setting of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate gels.

Experimental Procedure

The experimental procedure adopted was practically the same as employed by Prasad and Gogate. Varying amounts of the solutions of the two constituents of the gel-forming mixture were taken in two test-tubes and certain amount of distilled water was added so that the total volume of the gelating mixture was 8 c.c. in the case of stannic phosphate and thorium arsenate gels and 9 c.c. in the case of thorium phosphate and cerium phosphate gels. The two test-tubes were corked and kept in the thermostat for about 15 minutes. Then the contents of the test-tubes were mixed and the opacity readings were taken.

The results obtained with each of these gels are given below.

1. Thorium Phosphate Gels

They were prepared by the method of Prasad, Mehta and Parmar.² It was found that if a mixture of potassium phosphate and phosphoric acid is employed instead of phosphoric acid alone, the whole system is initially opaque and there is a change in transparency during gelation and the mixture sets into a very transparent gel in a short time. This method of preparing thorium phosphate gel was used and the following solutions were employed:

- (A) 6% solution of thorium nitrate (Kahlbaum).
- (B) 12% solution of potassium phosphate (Merck).
- (C) 1.6 N phosphoric acid.
- (D) 0.2 N HCl.

The results obtained during the gelation of thorium phosphate gels are shown by means of curves obtained by plotting the opacity in terms of observed deflections in cm. against time in minutes. The effects of the addition of different amounts of (A), (B) and (C) (D) and of methyl and ethyl alcohols on the opacity changes during the course of gel-formation were investigated.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to a mixture containing 0.5 c.c. of (B) and 0.3 c.c. of (C). The effect of phosphoric acid was studied by adding 0.1 to 0.5 c.c. of (C) to 0.5 c.c. of (B) before it was added to 4.5 c.c. of (A). The effect of HCl was studied by adding 0.2 to 0.8 c.c. of (D) to a mixture containing 0.5 c.c. of (B) and

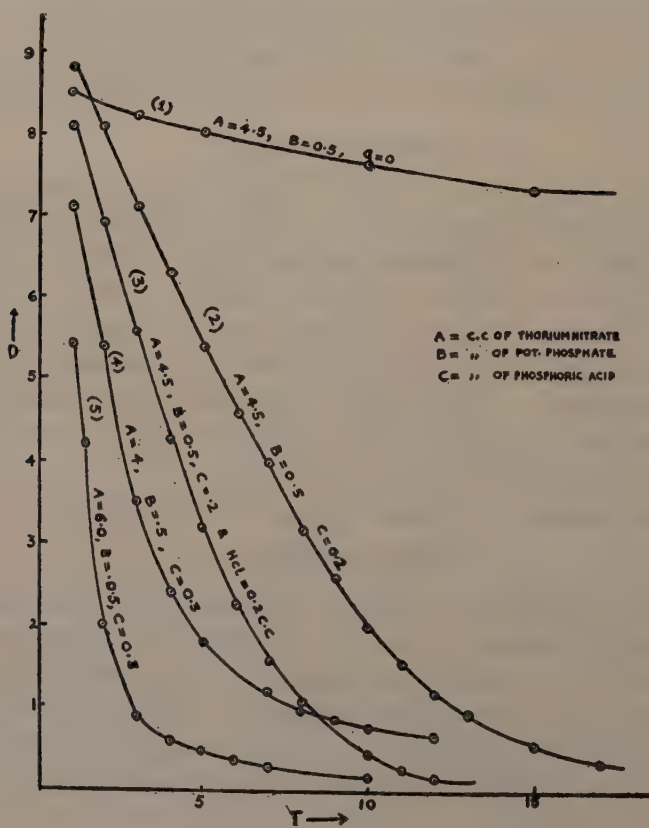


FIG. 1

0.2 c.c. of (C) before it was added to 4.5 c.c. of (A). The effect of ethyl alcohol was studied by adding 0.5 to 1.0 c.c. of ethyl alcohol to a mixture containing 0.5 c.c. of (B) and 0.3 c.c. of (C) before it was added to 4.5 c.c. of (A). The effect of methyl alcohol was studied by adding 0.5 c.c. to 1.5 c.c. of methyl alcohol to a mixture containing 0.5 c.c. of (B) and 0.4 c.c. of (C) before it was added to 4.5 c.c. of (A).

Some results indicating these effects are given in Figs. 1 and 2.

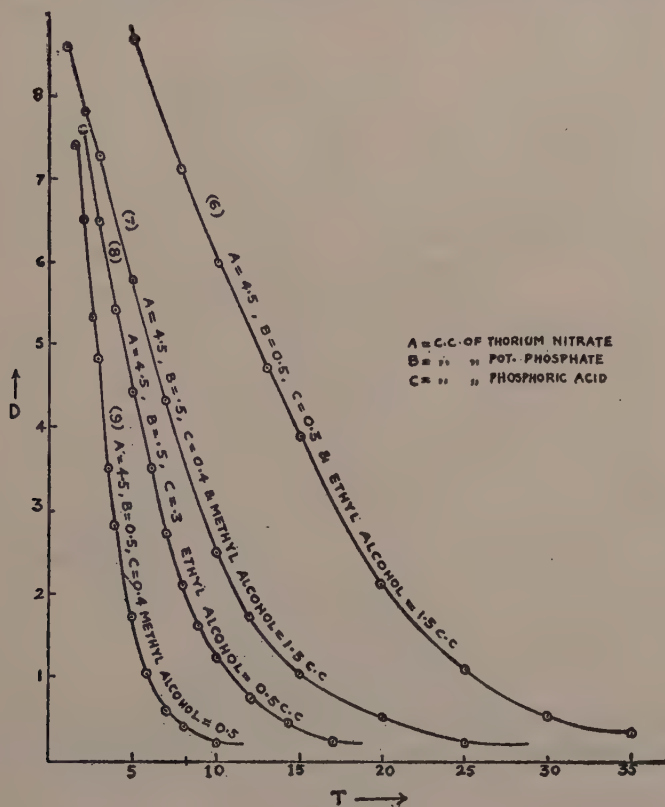


FIG. 2

2. Cerium Phosphate Gels

These gels were prepared by the method of Prasad and Desai.³ The following solutions were used:

- (A) 10% cerium nitrate.
- (B) 12% potassium phosphate.
- (C) 0.2 N HCl.

The effect of cerium nitrate was studied by adding 4.5 to 7.0 c.c. of (A) to 1.0 c.c. of (B). The effect of potassium phosphate was studied by adding

1.0 to 1.5 c.c. of (B) to 4.5 c.c. of (A). The effect of the addition of HCl was studied by adding 0.5 to 1.0 c.c. of (C) to 1.0 c.c. of (B) before it was added to 4.5 c.c. of (A). The effect of ethyl alcohol was studied by adding 1.0 to 2.0 c.c. of the same to 1.0 c.c. of (B) before it was added to 4.5 c.c. of (A).

Some results indicating these effects are given in Fig. 3.

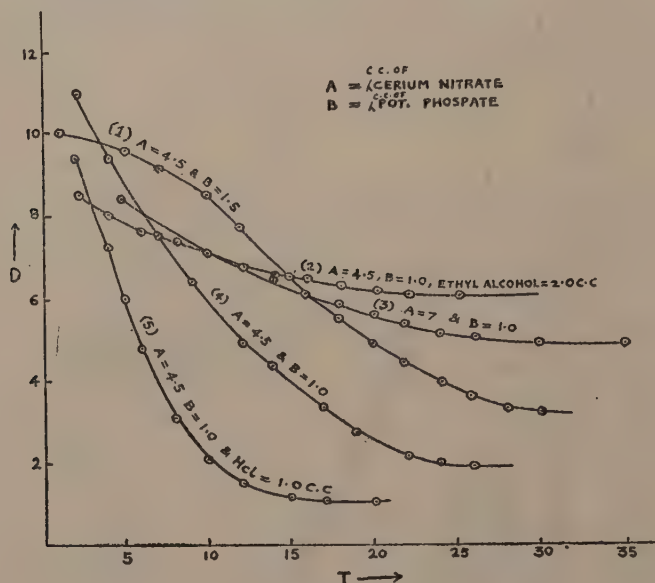


FIG. 3

3. Thorium Arsenate Gels

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

- (A) 6% thorium nitrate (Kahlbaum).
- (B) 10% solution of pyro-arsenic acid (extra pure Merck).
- (C) 2 N HCl.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to 0.54 c.c. of (B). The effect of pyro-arsenic acid was studied by adding 0.48 to 0.72 c.c. of (B) to 4 c.c. of (A). The effects of HCl, ethyl alcohol, methyl alcohol and glycerine were studied by adding 0.06 to 0.2 c.c. of (C), 0.2 to 0.4 c.c. of ethyl alcohol, 0.1 to 0.3 c.c. of methyl alcohol and 0.06 to 0.1 c.c. of glycerine to 0.54 c.c. of (B) before it was added to 4.0 c.c. of (A).

Some results indicating these effects are given in Fig. 4.

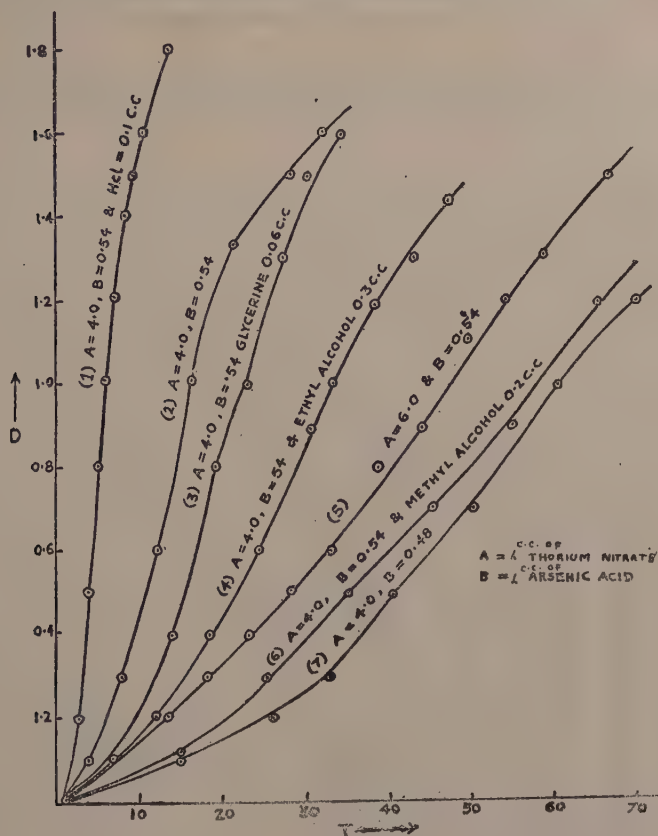


FIG. 4

4. Stannic Phosphate Gels

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

- (A) 43.82 g. of stannic chloride dissolved in 250 c.c. of distilled water in the presence of 1.0 c.c. of nitric acid to prevent hydrolysis.
- (B) 0.2 N phosphoric acid.
- (C) 2 N HCl.

The effect of stannic chloride was studied by adding 2.2 to 3.0 c.c. of (A) to 2.4 c.c. of (B). The effect of phosphoric acid was studied by adding 2.4 to 3.0 c.c. of (B) to 3.0 c.c. of (A). The effect of HCl was studied by adding 0.1 to 0.2 c.c. of (C) to 2.4 c.c. of (B), before it was added to 3.0 c.c. of stannic chloride. The effects of methyl, ethyl, propyl alcohols were

studied by adding 1.0 to 2.0 c.c. of methyl alcohol, 1.0 to 2.0 c.c. of ethyl alcohol and 1.0 to 3.0 c.c. of propyl alcohol, respectively to 2.4 c.c. of (B) before it was added to 2.4 c.c. of (A).

Some results indicating these results are given in Fig. 5.

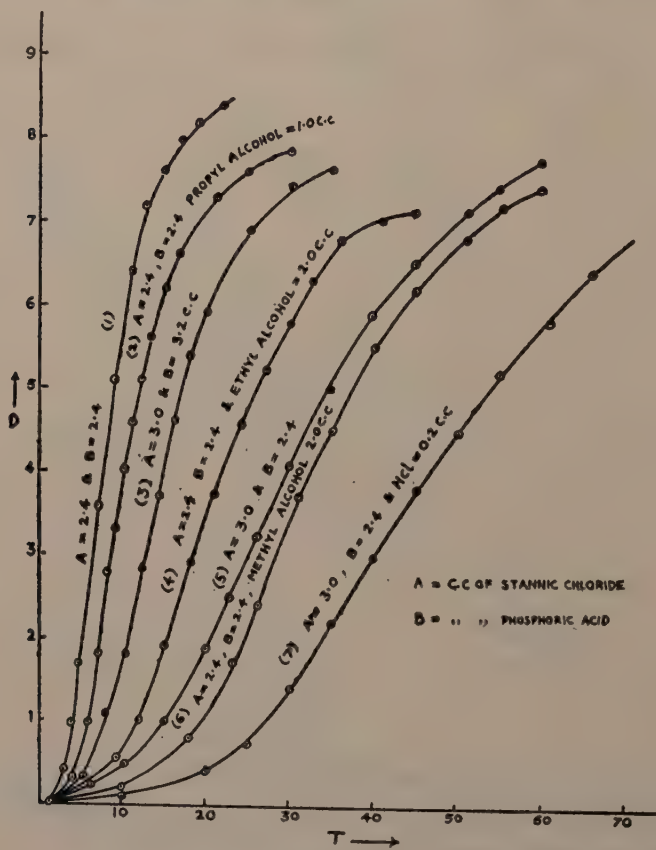


FIG. 5

5. Discussion of Results

All the results given above are reproducible and the experimental error is within ± 2 per cent. These results are therefore important as they represent accurately the changes in opacity taking place during the setting of the gels studied in this investigation. The time-deflection curves in all these cases are continuous and thereby indicate that gelation is a continuous phenomenon.

The results obtained in the case of each gel are discussed separately in the following.

1. Thorium Phosphate Gels—

The time-deflection curves (Figs. 1 and 2) show that the gels are opaque in the beginning. The opacity decreases during gel-formation and it reaches a constant value.

It will be noticed from the various curves in Fig. 1 that increasing amounts of thorium nitrate (curves 4 and 5), phosphoric acid (curves 1 and 2) and HCl (curves 2 and 3) in the gel-forming mixture increase the rate of change of opacity and make the gel more and more transparent. It is interesting to note that a small quantity of phosphoric acid is able to make the gel very transparent.

Non-electrolytes exercise a great influence on the course of gel-formation. Increasing amounts of methyl alcohol (curves 6 and 8) and ethyl alcohol (curves 7 and 9, Fig. 2) in the gel-forming mixture decrease the rate of change of opacity. In these cases there are no great changes in the final value of opacity.

In the case of these gels the plot of $\log d$ against t (d being the deflection at the time t), was found to be a straight line, showing thereby that $d = ae^{-kt}$.

2. Cerium Phosphate Gels—

These gels, like thorium phosphate gels, are opaque in the beginning and become transparent during setting (Fig. 3).

Increasing amounts of cerium nitrate (curves 3 and 4) and potassium phosphate (curves 1 and 4) decrease the rate of change of opacity and make the gel more and more opaque. However, increasing amounts of HCl increase the rate of opacity and make the gel more and more transparent (curves 4 and 5).

The effect of ethyl alcohol is the same as that of cerium nitrate; the rate of change of opacity is decreased and the gel becomes more and more opaque as the amount of alcohol in the gel increases (curves 2 and 4).

In the case of this gel also, $\log d$ plotted against t , was found to be a straight line, so that $d = ae^{-kt}$.

3. Thorium Arsenate Gels—

These gels are clear in the beginning and become opaque during setting as shown by the deflection-time curves (Fig. 4).

Increasing amounts of thorium nitrate (curves 2 and 5) decrease the rate of change of opacity, whereas increasing amounts of pyro-arsenic acid (curves 2 and 7) increase the rate. Increasing amounts of HCl increase

the rate of change of opacity (curves 1 and 2). Non-electrolytes employed are ethyl and methyl alcohols, and glycerine. Curves 2 and 4, 2 and 6, 2 and 3, respectively, show their effects. It will be seen that non-electrolytes decrease the rate of change of opacity.

4. *Stannic Phosphate Gels*—

The deflection-time curves in Fig. 5 show that the stannic phosphate gels are clear in the beginning and they increase in opacity during gel-formation and reach a constant value.

The rate of change of opacity is decreased by the addition of increasing amounts of stannic chloride to the gel-forming mixture (curves 1 and 5), whereas increasing amounts of phosphoric acid increase the rate of change of opacity (curves 3 and 5).

Increasing amounts of HCl decrease the rate of change of opacity (curves 5 and 7). Curves 1 and 6, 1 and 4, and 1 and 2 represent the effects of the addition of increasing amounts of methyl, ethyl and propyl alcohols to the gel-forming mixture. It will be seen that their addition causes the decrease in the rate of change of opacity of the gel-forming mixture.

One of the factors that causes the change of opacity is the change in the intensity of the scattered light by the gel-forming mixture with time. The intensity of light scattered by a colloid system is given by Lord Rayleigh's equation,⁴ which under standard and fixed conditions can be written as

$$I = kV^2 N,$$

where N is the number and V , the volume of the scattering particles. The observed changes in the opacity during gel-formation may be due to changes in these two factors during the setting of the gels.

Changes in the intensity of scattered light which cause changes in opacity may also be brought about by changes in the anisotropy, arrangement and distribution of the micelles in a gel as pointed out by Prasad and Gogate. It is quite probable that changes in the anisotropy, distribution and arrangement of the micelles in the gel taking place with the changes in the amounts of the constituents of the gel-forming mixtures may be responsible, to a great extent, for the rate of change of opacity and also for the final value reached at the completion of the gelation process.

Further work on the changes in the intensity and depolarisation factors of the light scattered by gels during and after gelation is in progress. From the total scattering observed an attempt is being made to separate the

scattering due to size, number and anisotropy and to study their changes during gelation.

The authors feel grateful to Dr. Mata Prasad, D.Sc., F.I.C., for suggesting the problem and for the guidance throughout the progress of this work.

6. *Summary*

The opacity changes during the formation of gels of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate have been investigated. Opacity-time curves, in the case of thorium and cerium phosphate gels, are exponential in character.

The changes in the opacity with time of the gels formed from different amounts of the constituents of the gel-forming mixture and the effects of HCl and non-electrolytes on the course of gel-formation have been investigated. In general non-electrolytes decrease the rate of change of opacity, while HCl increases the same.

The final values of opacity are not the same in all these cases but they vary with the concentration of the constituents of the gel-forming mixture. It has been suggested that the changes in the rate of changes of opacity and the final value of opacity may be due to the changes in the number, size, anisotropy, distribution and arrangement of the micelles taking place under the different conditions of the gel-formation.

REFERENCES

1. *Proc. Ind. Acad. Sci.*, 1943, **17**, 161.
2. *J. Indian Chem. Soc.*, 1936, **13**, 69-71.
3. *J. Univ. Bom.*, 1938-39, **7**, 148.
4. *Phil. Mag.*, 1899, **47**, 375.

EXCITATION PROCESSES IN THE NIGHT SKY AND THE AURORA

BY TA-YOU WU

(Department of Physics, National University of Peking, and Institute of Astronomy,
Academia Sinica, Kun-ming, China)

Received July 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction

OUR knowledge concerning the conditions prevailing in the upper atmosphere of the earth comes mainly from the following two sources: (1) From the behaviour of the ionized layers towards radio waves and the magnetic variations, it is possible to make certain estimates of the concentrations of electrons, heavy ions and neutral particles in the different layers. In the present work, we shall not be concerned with the various aspects of these problems. Suffice it to summarize the main results as follows¹:

	Electron density		Heavy ion density	Collision freq. of electron	Concentration of neutral particles
	Day	Night			
F layer 200-300 km. ..	$3 \times 10^5/\text{c.c.}$	$2 \times 10^5/\text{c.c.}$	$10^5\text{--}10^6/\text{c.c.}$	$6 \times 10^3/\text{sec.}$	$10^{12}/\text{c.c.}$
E layer 100 km. ..	$1.5 \times 10^6/\text{c.c.}$	$8 \times 10^3/\text{c.c.}$	$10^8/\text{c.c.}$	$2 \times 10^5/\text{sec.}$	$3 \times 10^{13}/\text{c.c.}$

The ionization and the dissociation of the atoms and molecules are due to the ultraviolet radiations from the sun. The rather slow falling off of the electron density after sunset and the much higher concentration of heavy ions than that of electrons, are due to the small probability of recombination between electrons and positive ions and the much more frequent occurrence of attachment process of electrons to neutral atoms and molecules, the former process taking place at the rate of about 10^{-5} per second and the latter about 1 per second at the pressure of the E layer.

(2) From the analysis of the spectra of the night sky and the aurora, it is found that in both cases the radiations consist of the forbidden lines of

¹ Cf. H. S. W. Massey, *Negative Ions*, 1938, Cambridge Univ. Press (1938), pp. 89-100. Later results are unfortunately not available to the writer, but they would not affect the discussions in the following.

[OI], the various band systems of N_2 and N_2^+ , some weak bands of O_2 and H_2O and some lines or bands of uncertain origin. There is a great difference, however, between the spectrum of the night sky and that of the aurora borealis, namely, the negative bands of N_2^+ are very strong in the latter but very weak in the former, while the Vegard-Kaplan bands of N_2 are very strong in the former but rather weak in the latter. In each individual band system, certain bands in certain sequences are particularly enhanced. Evidently a clear understanding of the excitation mechanisms of these radiations will contribute greatly to our knowledge of the conditions in the upper atmosphere of the earth. For convenience of the discussion, we shall summarize the main features of the spectra of the night sky and the aurora as follows²:

(a) *The forbidden lines of [OI].*—The green line at 5577 Å is by far the most intense line in the spectrum of the night sky and is also very intense in the aurora. The red lines at 6300 and 6364 Å are inferior in intensity in both cases, but are still fairly strong compared with the other bands in each spectrum. In the night sky, the green line increases very slowly in intensity and reaches a maximum towards midnight after which it decreases slowly again.^{3,4} The red lines on the other hand have the greatest intensity immediately after sunset and fall off gradually in the night.⁴ In the sunlit aurora, the red lines are found to be greatly enhanced relative to the green one.⁵

(b) *First negative bands of N_2^+ .*—In the aurora spectrum, the following negative bands of N_2^+ are very intense³:

4708 Å ($v' = 0 \rightarrow v'' = 2$), 4278 Å ($v' = 0 \rightarrow v'' = 1$), 3914 Å ($v' = 0 \rightarrow v'' = 0$).
 4648 (. 1 \rightarrow 3), 4236 (. 1 \rightarrow 2),
 4199 (. 2 \rightarrow 3),

The 4708, 4278 and 3914 bands have comparable or even greater intensities than the green 5577 line in the ordinary aurora, and become very much more intense than the latter in sunlit aurora.^{2,4} In the night sky, perhaps only the 3914 band can be identified with certainty.⁴

(c) *Vegard-Kaplan bands of N_2 .*—In the night sky spectrum, the radiations next in intensity to the forbidden lines of [OI] are the Vegard-Kaplan

² For a summary of the facts concerning the spectra of the aurora and the night sky, see, respectively, E. W. Hewson, *Rev. Modern Physics*, 1937, 9, 403; and G. Dejardin, *ibid.*, 1936, 8, 1, and references given there.

³ Cf. G. Dejardin, *loc. cit.*

⁴ C. T. Elvey, P. Swings and W. Linke, *Astrophys. Jour.*, 1941, 93, 337.

⁵ L. Vegard and E. Tonsberg, *Nature*, 1936, 137, 778.

bands of N_2 . The bands observed by Sommer, Cabannes³ and Elvey, Swings and Linke⁴ are summarized in Table I.

TABLE I
Vegard-Kaplan Bands in the Night Sky

	v''	10	11	12	13	14	15	16	17	18
v'										
0		3598	3889	4220	4603	5062				
1		3425	3707	3984	4316	4719				
2			3501	3787	4073	4420	4827	5324		
3				3582	3855	4174	4543	4962		
4					3664	3949	4270	4650		
5						3742	4048	4379	4768	
6							3834	4144	4493	
7					3211?	3424?		3936	4259	4616

Of these, the 4073, 4171, 4270, 4420, 4543 and 4827 bands from the levels $v' = 2, 3, 4$ are the most intense. In the aurora spectrum, some 10 stronger ones of these bands have also been identified, although they are in general very weak.⁶

(d) *First positive bands of N_2* .—In the aurora spectrum, the bands observed by Vegard at 6323 and 7880 Å have been identified with the $v' = 10 \rightarrow v'' = 7$ and $v' = 7 \rightarrow v'' = 6$ transitions respectively. In the spectrum of the night sky, a number of first positive bands has been found, the more intense ones being those from the vibrational levels $v' = 7$ and 15 according to Cabannes.³ More recently, Elvey, Swings and Linke have identified from their own and Babcock's observations the following bands ($4 \rightarrow 1$), ($7 \rightarrow 4$), ($8 \rightarrow 4$), ($8 \rightarrow 5$), ($9 \rightarrow 6$), ($10 \rightarrow 4$), ($10 \rightarrow 5$), ($11 \rightarrow 5$), ($11 \rightarrow 8$), ($12 \rightarrow 7$), ($12 \rightarrow 8$), ($13 \rightarrow 8$), ($13 \rightarrow 9$), ($14 \rightarrow 9$), ($15 \rightarrow 11$), ($16 \rightarrow 12$). These are weak compared with the Vegard-Kaplan bands.

(e) *Second positive bands of N_2* .—In the aurora, the sequences $v'' - v' = -1, 0, 1, 2, 3, 4$, with v' from 0 to 5 and 6, are observed. They are weak compared with the negative bands of N_2^+ . In the night sky, the bands of the second positive system are very weak. Cabannes found the bands 4574 Å ($v' = 1 \rightarrow v'' = 6$), 4059 Å ($v' = 0 \rightarrow v'' = 3$), 3998 Å ($v' = 1 \rightarrow v'' = 4$). On the other hand, these bands do not appear in Elvey, Swings and Linke's spectrograms. These authors found instead only the 3159 ($1 \rightarrow 0$) and the 3371 ($0 \rightarrow 0$) bands; even then the identifications are not certain since each

⁶ Cf. J. Kaplan, *Phys. Rev.*, 1938, **54**, 198, and reference given to the works of Vegard.

of these bands can be equally well ascribed to other transitions in other band systems.

(f) *Lyman-Birge-Hopfield bands of N_2* .—The existence of bands of this system, especially those from $v' = 0$ to $v'' = 19 - 23$, has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.⁴

(g) *Atmospheric bands of O_2* .—The observations and analysis of Cabannes seem to suggest the existence of the A, B, a , a' , a'' , bands of O_2 at 0.76μ , 0.69μ , 0.63μ , 0.58μ , 0.54μ , corresponding to the transitions $0 \rightarrow 0$, $1 \rightarrow 0$, $2 \rightarrow 0$, $3 \rightarrow 0$, $4 \rightarrow 0$ respectively.³ On the other hand, from Babcock's and their own observations, Elvey *et al.* concluded that probably only the a' band is present in the spectrum of the night sky.⁴

(h) *Schumann-Runge bands of O_2* .—Elvey, Swings and Linke showed from their own observations, and Kaplan from those of Gauzit, that the positions of certain ultraviolet bands in the night sky agree quite well with the transitions $v' = 0$, $1 \rightarrow v'' = 12 - 18$, in the Schumann-Runge system and suggested their probable presence.

(i) *The yellow lines of Na*.—The yellow lines of Na have been observed by Bernard, Cabannes and others at 5893 Å in the spectrum of the night sky.⁷ They are not observed in the aurora.

(j) *Water vapour bands*.—The observations and analysis of Cabannes³ seem to suggest strongly the presence of the water vapour bands at 0.59μ , 0.65μ , 0.698μ , and 0.72μ . On the other hand, from their own and Babcock's observations, Elvey, Swing and Linke concluded that probably only the 0.65μ band is present in the spectrum of the night sky and regarded the problem of water vapour bands in the night sky as unsettled.

In addition to these, there are some weaker lines or bands of uncertain origin in both the spectrum of the night sky and that of the aurora. But undoubtedly the above-mentioned radiations are the most important features in both cases.

To explain the cause of the auroræ, their shapes and spectral characteristics, many theories have been proposed. A common feature of the more successful ones is that the emission of radiations of the aurora is excited by swift particles which may be directly ejected from the sun, or may be secondary particles resulting from these corpuscular rays or from ionization of the uppermost atmosphere by sudden outbursts of ultraviolet

R. Bernard, *Astrophys. Jour.*, 1939, 89, 133; J. Cabannes, J. Dufay and J. Gauzit, *ibid.*, 1939, 88, 164, and references to earlier papers given in these papers.

radiations from the sun. These theories, while successful in furnishing a source of energy for excitation and explaining the forms of the auroræ, and their concentration near the poles, cannot account for the selective nature of the excitations of the various radiations, and in particular, for the enhancement of certain bands in a system. Corpuscular rays, whatever they may be, must be expected to have a certain spread in energy; and as the excitation functions of atomic and molecular transitions by electron impact do not possess sharp maxima in general, one would expect more or less non-descript rather than the highly selective excitations observed. Also the complete absence of radiations corresponding to the allowed transitions in the atoms of N, O, He and H would be difficult to understand,⁸ as the difference between the excitation potentials of these atoms and those of the observed lines and bands would be small compared with the energies available in the corpuscular rays. Hence it appears that while these theories may be correct in dealing with the large-scale features, the corpuscular rays cannot be solely responsible for the excitations of the radiations in the aurora and in the night sky.

Towards the understanding of the nature of the mechanism in the excitation processes in the upper atmosphere, considerable progress on the experimental side has been made by Kaplan by reproducing very closely the various spectral characteristics of the aurora and the night sky by running electrical discharges and afterglows under special conditions in the laboratory.⁹ Thus he found that it is possible to produce the green [OI] line, the Vegard-Kaplan bands and other bands of N_2 and N_2^+ in various relative intensities by varying the conditions of the discharge. The production of the Vegard-Kaplan bands not only shows that the metastable $N_2(A^3\Sigma)$ molecules are present but suggests that they may play an important rôle in the excitation of the other bands. In fact it is possible to explain the enhancement of the bands from $v' = 6, 7$ and $v' = 10, 11$ in the first positive system of N_2 in an afterglow in active nitrogen as the result of collisions of the second kind Q_{10} and Q_9 in Table II. While these

⁸ We believe that the absence of the He and H lines in the aurora and the night sky is no argument against the presence of He and H in the upper atmosphere, but means that the excitation condition there is not adequate for the production of the lines of He and H as well as those of N and O. In fact, there is some indication, although uncertain, for the presence of two NH bands 3371 Å ($0 \rightarrow 0$) and 3360 Å ($1 \rightarrow 1$) in the night sky, according to Kaplan, *Phys. Rev.*, 1939, 55, 593, and Elvey, Swings and Linke, *loc. cit.* If these identifications are correct, they would indicate the presence of atomic H in the upper atmosphere, which forms NH on combining with the N atoms.

⁹ Kaplan's experiments are reported in various issues of the *Physical Review* and the *Nature* from 1928 to the present day.

experiments are exceedingly valuable in throwing considerable light on the problem, one cannot immediately identify the conditions in the upper atmosphere with those in the discharge tubes. In the latter, excitations by electron impact play a rôle that cannot be ignored, while in the upper atmosphere excitations by electron impact become impotent on account of the low energies of the free electrons, unless one invokes high energy electrons in corpuscular rays, in which case one introduces the difficulty with the selective excitations discussed above. The considerable difference in pressure in the discharge tube and in the upper atmosphere is another factor that must be reckoned with, since the question whether a forbidden transition radiates or not depends on the frequency of quenching collisions, which is in turn determined by the concentration of the appropriate colliding particles. Even the walls of the discharge tube constitute a great difference from the atmosphere, since they furnish the most efficient third-body for the formation of metastable molecules on recombinations between the atoms, while a three-body collision becomes a rare event in the upper atmosphere on account of the low pressure there.

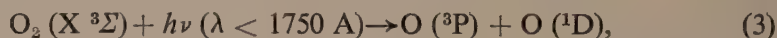
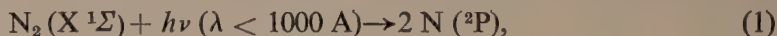
On the theoretical side, many theories have been proposed for the excitation mechanisms in the upper atmosphere, among which the one due to Chapman seems to be most favoured by many authors.¹⁰ According to it, the source of energy of the radiations in the night sky is the energy of dissociation of the oxygen molecules stored up during the day, and the radiations of the O atom and the N₂ molecule are excited when two O atoms recombine in their neighbourhood in a three-body collision. We shall show in the following that the frequency of occurrence of such three-body collisions is entirely much too low to account for the observed intensities of the various radiations and that the theory is inadequate in explaining the diurnal intensity variations of the most prominent radiations in the night sky.¹⁶ It is proposed to show that the main spectral features, especially of the night sky, can be satisfactorily understood on the view that the key processes are the formation of the metastable molecules of oxygen and nitrogen by radiative recombinations between the atoms generated during the day, and the excitation processes are then the various collisions of the second kind, of the resonance type, between the metastable molecules and atoms. It is important that any suggested mechanisms be not judged on energetic considerations alone; it is necessary to pay a closer attention to the

¹⁰ S. Chapman, *Phil. Mag.*, 1937, **23**, 657. Most unfortunately this journal is not available either in Kun-ming or in Chungking; but from another paper by Chapman, *Astrophys. Jour.*, 1939, **90**, 309, and a paper by Cabannes, *Comptes Rendus*, 1939, **208**, 1770, it is gathered that only dissociation of O₂ and three-body recombinations are considered.

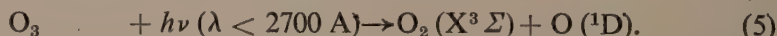
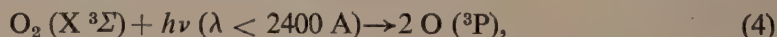
rates at which the various processes might take place in the upper atmosphere and to see if they may account for the observed intensities of the radiations. For this a closer discussion of the probabilities of the various processes is necessary.

Theory

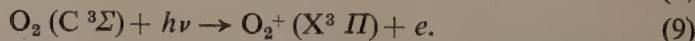
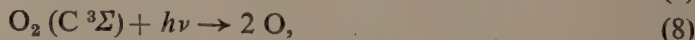
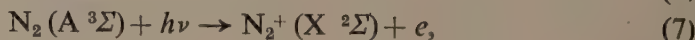
We shall start with an atmosphere that is composed mainly of N_2 , a smaller amount of O_2 , some rare gases and some water vapour, and assume that as the result of dissociation and ionization of the N_2 and O_2 molecules by the ultraviolet solar radiations, there are also present N and O atoms, N_2^+ and O_2^+ ions as well as N^+ and O^+ ions. These ions, the electrons and the negative ions formed by the attachment of electrons to neutral atoms and molecules do not play any direct rôle in the excitation processes in the theory and hence will be ignored in the following. The primary processes are:



and to a less extent and in the lower atmosphere,



Positive ions may be produced by the photo-ionization of the N_2 and O_2 molecules and the atoms, by solar radiations of very short wave-length; but it is also possible that the metastable $N_2(A^3\Sigma)$ and $O_2(C^3\Sigma)$ formed from the N and the O atoms by the processes, Q_1 , Q_3 , Q_2 , Q_4 in Table II contribute greatly to the ionization by absorption of ultraviolet radiations of longer wave-length and hence of greater abundance in the solar radiations.



The ionization potentials in (7) and (9) are 9.7 and 7.5 volts respectively compared with the 13.6 and 14.5 volts respectively for the O and N atoms. It is not necessary to exclude the possibility that some dissociation and ionization are effected by agents other than ultraviolet radiations; but as we shall immediately see, on account of the low probabilities for either the radiative or the three-body recombination, the atoms produced in the day by the processes (1), (2), (3), (6) and (8) will disappear slowly enough to account for the rôle they are assumed to play in the night sky. In fact,

for this purpose alone, it is not necessary to invoke the action of agents other than the solar radiations.

On the assumption that there are present in the upper atmosphere the atoms and molecules of N and O but no radiations to remove the meta-stable $N_2(A^3\Sigma)$ and $O_2(C^3\Sigma)$, as it is the case after sunset, the various processes in Table II are possible. In the following we shall assess their plausibilities. The actual contribution of a given process depends of course, besides on the intrinsic probability of the process, also on the concentrations of the particles involved.

Of these processes, $Q_6, Q_7, Q_7', Q_7'', Q_8, Q_9, Q_9', Q_9'', Q_{10}, Q_{10}', Q_{11}, Q_{12}, Q_{12}', Q_{13}, Q_{14}, Q_{15}, Q_{16}, Q_{17}$ are collisions of the second kind in which the energy of electronic excitation of one particle is transferred into the energy of electronic and vibrational excitation of a molecule. In these cases, the resonance is very close since the vibrational levels are only 1/5 to 1/4 of a volt apart. In Table II the vibrational level which is excited with the

TABLE II
Excitation Processes in the Upper Atmosphere

Notation	Process	Radiation excited
Q_1	$N(^4S) + N(^4S) + X \rightarrow X + N_2(A^3\Sigma), \nu \text{ up to } 7$	Vegard-Kaplan
Q_2	$O(^3P) + O(^3P) + X \rightarrow X + O_2(C^3\Sigma),$	Herzberg bands
Q_3	$N(^4S) + N(^4S) \rightarrow N_2(A^3\Sigma) + h\nu$	Vegard-Kaplan
Q_4	$O(^3P) + O(^3P) \rightarrow O_2(C^3\Sigma) + h\nu$	Herzberg bands
Q_5	$O_2(C^3\Sigma) + O_2(C^3\Sigma) \rightarrow O_2(X^3\Sigma) + O(^3P) + O(^1S) + 0.12$	Green [OI]
Q_5'	$\rightarrow 2 O(^1D) + 0.37 \text{ volt}$	Red [OI]
Q_6	$2N_2''(A^3\Sigma) \rightarrow N_2''(X^1\Sigma) + N_2''(C^3\Pi), \nu \text{ up to } 5$	2nd positive
Q_6'	$\rightarrow 2N(^2D) + 0.1 \text{ volt}$	
Q_6''	$\rightarrow N(^4S) + N(^2P) + 1.3 \text{ volt}$	
Q_7	$N_2''(A^3\Sigma) + O(^1S) \rightarrow O(^3P) + N_2(B^3\Pi), \nu = 15$	1st positive
Q_7'	$\rightarrow O(^1D) + N_2(B^3\Pi), \nu = 9$	Lyman-Birge-Hopfield
Q_7''	$\rightarrow O(^3P) + N_2(B^3\Pi), \nu = 5$	1st positive
Q_8	$N_2''(A^3\Sigma) + O(^1D) \rightarrow O(^3P) + N_2(B^3\Pi), \nu = 3, 4$	" "
Q_9	$N_2''(A^3\Sigma) + N(^2P) \rightarrow N(^4S) + N_2(B^3\Pi), \nu = 11$	" "
Q_9'	$\rightarrow N(^2D) + N_2(B^3\Pi), \nu = 6$	Lyman-Birge-Hopfield
Q_9''	$\rightarrow N(^4S) + N_2(B^3\Pi), \nu = 0$	1st positive
Q_{10}	$N_2''(A^3\Sigma) + N(^2D) \rightarrow N(^4S) + N_2(B^3\Pi), \nu = 6$	" "
Q_{10}'	$\rightarrow N(^2D) + N_2(B^3\Pi), \nu = 0$	Lyman-Birge-Hopfield
Q_{11}	$N_2''(A^3\Sigma) + O_2''(X^3\Sigma) \rightarrow N_2''(X^1\Sigma) + O_2(B^3\Sigma), \nu = 0$	Schumann-Runge
Q_{12}	$N_2''(A^3\Sigma) + O_2(C^3\Sigma) \rightarrow O_2(X^3\Sigma) + N_2(C^3\Pi), \nu = 0$	2nd positive
Q_{12}'	$\rightarrow N_2(B^3\Pi), \nu = 20$	1st positive
Q_{13}	$N_2''(A^3\Sigma) + N_2''(X^2\Sigma) \rightarrow N_2''(X^1\Sigma) + N_2''(B^2\Sigma), \nu = 11$	1st negative
Q_{14}	$N_2''(X^2\Sigma) + N(^2P) \rightarrow N(^4S) + N_2''(B^2\Sigma), \nu = 1$	" "
Q_{15}	$N_2''(X^2\Sigma) + O(^1S) \rightarrow O(^3P) + N_2''(B^2\Sigma), \nu = 3$	" "
Q_{16}	$O_2(X^3\Sigma) + O(^1D) \rightarrow O(^3P) + O_2(A^1\Sigma), \nu = 2$	A, B, a bands of O_2
Q_{17}	$O_2(X^3\Sigma) + N(^2D) \rightarrow N(^4S) + O_2(A^1\Sigma), \nu = 4$	α', α'' bands of O_2
Q_{18}	$O(^3P) + N(^2D) \rightarrow O(^1D) + N(^4S) + 0.41 \text{ volt}$	Red [OI]
Q_{19}	$O(^1D) + N(^2D) \rightarrow O(^1S) + N(^4S) + 0.16 \text{ volt}$	Green [OI]
Q_{20}	$Na(^2S) + N(^2D) \rightarrow Na(^2P) + N(^4S) + 0.27 \text{ volt}$	Yellow lines Na
Q_{21}	$Na(^2S) + O(^1S) \rightarrow Na(^2P) + O(^1D) + 0.11 \text{ volt}$	" " "
Q_{22}	$Na(^2S) + O(^1D) \rightarrow Na(^2P) + O(^3P) + 0.14 \text{ volt}$	" " "
Q_{23}	$N_2(X^1\Sigma'') + H_2O \rightarrow N_2(X^1\Sigma') + H_2O'$	Water vapour bands

closest resonance is given. The cross-sections of the processes are, however, not solely determined by energy considerations alone. A theoretical evaluation of the cross-sections of such processes is very difficult, as they depend on the coupling between the electronic and the nuclear motions of the molecule. Some rough idea about the order of magnitude of the probabilities of such processes may be obtained from the experiments of Zemansky in which the cross-sections for the de-excitation of $\text{Hg } ^3\text{P}_1 \rightarrow ^3\text{P}_0$ by energy transfer to the vibrational motion of a colliding molecule are found to be of the order of the gas kinetic values.¹¹ The processes concerned here involve also the excitation of electronic states; their cross-sections may be smaller than the gas kinetic values when the spin rule is violated, but may be of the same order as the latter when the spin rule is satisfied. In the latter category we have Q_7' , Q_7'' , Q_9' , Q_9'' , Q_{10}' , Q_{12} , Q_{12}' , Q_{16} , Q_{17} .

The processes Q_{18} to Q_{22} involve the transfer of purely electronic energies and hence may have very large cross-sections for very close resonance. Their exact values are not known, but it is probable that they lie between 10^{-2} and 10^4 times the gas kinetic values when the spin rule is satisfied and have small values when it is not.¹² Thus of the three processes Q_{20} , Q_{21} , Q_{22} for the excitation of the yellow lines of Na, Q_{21} is by far the most probable both because of the small energy discrepancy and the spin rule.

The processes Q_5 , Q_5' , Q_6' , Q_6'' represent the dissociation of a molecule on collision with another, the energy being furnished, not by the kinetic energy of relative motion, but by the energies of excitation of both molecules. There is involved a transfer of electronic energy to the kinetic energy of the resulting particles and for this reason the cross-sections will be large only when there is very close resonance, *i.e.*, when the amount of energy to be transformed into the kinetic energy of the heavy particles is small. Thus the cross-section of Q_5 may be expected to be very large compared with the others since the spin rule is satisfied and the energy discrepancy is small.

Consider next the radiative processes such as Q_4 . If the final state can combine with the quasi-state formed by the close approach of the two atoms

¹¹ Zemansky, *Phys. Rev.*, 1930, **36**, 919.

¹² For processes involving the transfer of electron and electronic energy, reference may be made to the experimental work of Manley and Duffendack, *Phys. Rev.*, 1935, **47**, 56, and of Duffendack and Gran, *ibid.*, 1937, **51**, 804. These show that the cross-section of a process in which a neutral atom is simultaneously ionized and excited on collision with a positive atomic ion may be as large as 10^4 – 10^5 times the gas kinetic value when the resonance is close. For processes involving the transfer of electronic energy alone, there is the theoretical work of Kallmann and London, *Zeits. f. phys. Chem.*, 1929, **B 2**, 220, but no experimental work seems available. It is probable that the cross-sections are of the same order as those above.

by dipole transitions, the cross-sections may be estimated on general considerations at 10^{-7} — 10^{-5} times the gas kinetic values for slow atoms,¹³ and are hence small compared with those of the resonance collisions of the second kind. That they cannot be omitted from our considerations is due to the fact that they are still the chief mechanisms for the recombination of atoms in the upper atmosphere and are the source of energy of the excitation and radiation processes in the night sky, and possibly to a certain extent in the aurora. The other recombination processes, namely, three-body collisions such as Q_1 , have even smaller probabilities at the low pressure of the upper atmosphere. The probability of a three-body process may be expressed in terms of a cross-section for unit concentration of the third body, namely, $q \simeq \pi r^2 \cdot r/\lambda$, where r is the atomic dimension and λ is the mean free path of the recombining particles for unit concentration of the third body.^{13a} Obviously λ depends on the cross-section of the energy transfer from the recombining particles to the third body. Assuming, for the optimum case, that there is resonance in this transfer so that the cross-section may be as large as 10^3 times the gas kinetic value, one obtains for λ a value 10^{13} cms. and then $q \simeq 10^{-37}$ cm.⁵ Hence for the three-body collisions to be as frequent as the radiative recombinations, the concentration of the third body must be as high as 10^{15} per c.c. or greater. This value is about 10^2 to 10^3 times greater than the concentration at the E layer. Hence in the upper atmosphere, radiative recombinations are far more important than three-body processes, although in the lower atmosphere and in all laboratory experiments the reverse is the case.

Finally, in order that excitation collisions between metastable atoms and molecules be of any importance, it is necessary that de-excitations of the metastables by collisions with atoms and molecules be negligible. Now the latter process involves the transfer of electronic energy to the kinetic energies of the heavy particles (atoms and molecules); its probability can be calculated by means of the principle of detailed balancing from the probability of a process in which the electronic state of an atom or a molecule is excited by heavy particles in a collision of the first kind. As shown by Massey and Smith,¹⁴ the probabilities of excitation of the 2^1P state of He by protons are extremely small for proton energies below 400 volts. On general considerations, one would expect the probabilities of excitation of metastable states

¹³ Cf. Massey, *Negative Ions*, pp. 32–36; 78–79. As the number of molecular states arising from two atoms in given atomic states is very large, for a given state of the molecule it is in general possible to find a quasi-state having the correct symmetry properties so as to combine with the state by dipole transitions.

^{13a} J. J. Thomson, *Phil. Mag.*, 1924, 47, 337; cf. Massey, *Negative Ions*, pp. 38–39; 79–80.

¹⁴ Massey and R. A. Smith, *Proc. Roy. Soc.*, 1933, A 142, 142.

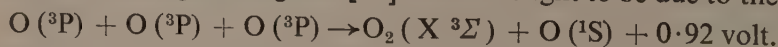
(i.e., optically forbidden transitions) by heavy particles to be even smaller. The principle of detailed balancing then requires that the probabilities of the reverse processes, namely, the de-excitation of metastable states by heavy particles, be also extremely small, especially for the kinetic energies of atoms and molecules with which we are concerned in the upper atmosphere. It is because of these extremely low probabilities of de-excitations by atoms and molecules and the comparatively high concentrations of the metastables that the collision processes in Table II, which are mostly of the resonance type, assume relatively great importance in the upper atmosphere.

From the above discussions, however, it would appear that nothing quantitative can be said concerning the probabilities of the various processes in Table II. Fortunately, most of our arguments in the following do not depend very critically on the exact values of these probabilities, although a more exact knowledge about them will enable one to make closer estimates of the concentrations of the various atoms and molecules and is hence greatly to be desired.

Consider now the various radiations in the spectra of the night sky and of the aurora in the light of the processes in Table II. In the following we shall denote the concentration of the atom, say, O (1S), by $[O\ ^1S]$, and the number of collisions, say, $O\ (^1D) + N\ (^2D) \rightarrow O\ (^1S) + N\ (^4S)$, in unit volume per second by $Q_{19}\ [O\ ^1D]\ [N\ ^2D]$ so that Q_{19} represents the cross-section of the process multiplied by the relative velocity of the colliding particles. For the three-body processes, q represents the cross-section for unit concentration of the third body.

(A) *Green [OI] line: $^1S \rightarrow ^1D$*

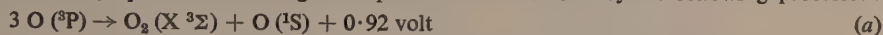
Since the green [OI] line is the most prominent line in both the spectra of the night sky and of the aurora, any theory must not fail to provide a satisfactory mechanism for the excitation of the line. From the earliest experiments of Kaplan in which the green line was excited in an afterglow in active nitrogen containing a small amount of oxygen, the suggestion was made that the 1S state is excited from the normal state 3P by the metastable atom N (2P).¹⁵ This explanation is now untenable since the energy available in N (P) is far short of being able to effect this excitation. Chapman and later Cabannes suggested that the various radiations of the night sky are excited by the recombinations between the oxygen atoms in the neighbourhood of another atom or molecule.¹⁰ For example, the green [OI] line is thought to be due to the process



¹⁵ J. Kaplan, *Phys. Rev.*, 1929, 33, 154.

It can be shown, however, that even on making the most optimum assumption about the probability of the three-body process, the frequency of its occurrence is far too low to account for the observed intensity of the green line.¹⁶ Also the suggested mechanism fails to account for the observed diurnal variations in the intensity of the [OI] lines.¹⁶ For the same reason,

¹⁶ According to Cabannes, *Comptes Rendus*, 1939, 208, 1770, who favoured Chapman's theory, the green [OI] line and the Vegard-Kaplan bands are excited by the following processes :



While these processes are energetically possible, we shall show that they are far too infrequent to account for the observed intensities of the radiations and that they fail to account for the observed diurnal variations in the intensities of the radiations.

(1) The probability of the process (a) is certainly very small if the energy excess 0.92 volt must be transformed into the kinetic energies of the resulting particles. It may be somewhat greater if this energy excess is retained as energy of vibrational excitation of the $\text{O}_2 (\text{X } ^3\Sigma)$ molecule. Even then, the probability must be very much smaller than the gas kinetic value since the spin rule is not satisfied in this case. Assuming, for the optimum situation, that it is of the same order as the gas kinetic value, then the cross-section q for unit concentration of the third body is $\approx 10^{-40} \text{ cm}^5$. With this value of q , even a concentration of $10^{11}/\text{c.c.}$ for $\text{O } (^3\text{P})$ would generate $\text{O } (^1\text{S})$ by the process (a) only at the rate of about 1 per c.c. per second. This is too small to account for the observed intensity of the green line, which calls for some $10^2 \text{ O } (^1\text{S})$ per c.c. Higher concentrations for $\text{O } (^3\text{P})$ are not available above the E layer, and according to Cabannes and Dufay, the radiations of the night sky come from above the E layer.

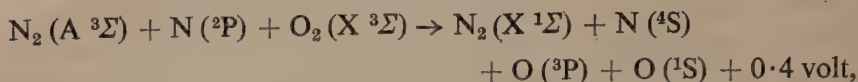
(2) Similar considerations show that no three-body processes are adequate in providing for a high enough concentration of $\text{O } (^1\text{D})$ to account for the intensities of the red [OI] lines.

(3) If the green [OI] line is excited by the process (a), then as the concentration of $\text{O } (^3\text{P})$ decreases, the rate of production of $\text{O } (^1\text{S})$ would also decrease. This would mean a continual decrease, however slow, in the intensity of the green line in the night. Also, if the $\text{O } (^1\text{D})$ are supposed to be produced as the result of the emission of the green line, then on account of the longer lifetime of the $\text{O } (^1\text{D})$, the concentration of $\text{O } (^1\text{D})$ would first increase until the rate of production is balanced by the rate of disappearance by the emission of the red lines and by other quenching collisions. This would mean that the red lines increase in intensity immediately after sunset and reach a constant value shortly afterwards. But these are just opposite to the observed variations, namely : the green line increases in intensity after sunset to a maximum near midnight, and the red lines are most intense immediately after sunset and decline in intensity thereafter.

(4) If the $\text{N}_2 (\text{A } ^3\Sigma)$ responsible for the emission of the Vegard-Kaplan bands are excited by the process (b), then, assuming again for the sake of argument the optimum value $q \approx 10^{-40} \text{ cm}^5$ for the cross-section of the process for unit concentration of the third body $\text{N}_2 (\text{X } ^3\Sigma)$, one would need a concentration of $10^{10}/\text{c.c.}$ for $\text{O } (^1\text{D})$, of $10^{11}/\text{c.c.}$ for $\text{O } (^3\text{P})$ and $10^{12}/\text{c.c.}$ for $\text{N}_2 (\text{X } ^1\Sigma)$ in order to produce one $\text{N}_2 (\text{A } ^3\Sigma)$ molecule per c.c. per second. Such a rate of production of $\text{N}_2 (\text{A } ^3\Sigma)$ is much too low to account for the observed total intensity of the Vegard-Kaplan bands, although the requisite concentration of $\text{O } (^1\text{D})$ is already neither provided for by any process nor consistent with the observed intensity of the red lines.

The above estimates are made on the assumption that the cross-sections for the three-body processes have the gas kinetic values. When account is taken of the fact that the cross-sections are probably very much smaller than the gas kinetic values, the inadequacy of the mechanisms such as (a) and (b) becomes even more obvious.

the suggestion that the molecule of O_2 is dissociated into the atoms $O(^3P)$ and $O(^1S)$ by active nitrogen,¹⁷ namely,



is unsatisfactory. Here we suggest the process Q_5 as the main process for the production of $O(^1S)$. That the metastable $O_2(C^3\Sigma)$ should play the important intermediate rôle is not implausible if one remembers that the metastable $N_2(A^3\Sigma)$ molecules are known to play a fundamental rôle in the upper atmosphere and the laboratory afterglow (as shown by the emission of the Vegard-Kaplan bands), and that the metastable $O_2(C^3\Sigma)$ bears a similar relation to processes involving the oxygen atoms and molecules as $N_2(A^3\Sigma)$ to those of nitrogen.

From the measured intensity of the green line in the night sky, Rayleigh has estimated that it corresponds to approximately 10^8 transitions per second in a column of the atmosphere of 1 sq. cm. base.¹⁸ This, together with the transition probability $A_{\text{green}} \simeq 2/\text{sec.}$,¹⁹ requires that there be at least some 10^2 $O(^1S)$ atoms produced per c.c. per second during the night. Assuming now that these are supplied by the process Q_5 , we have

$$Q_5 [O_2 C^3\Sigma]^2 \geq 10^2/\text{sec. c.c.}$$

Then, for a value of the cross-section of Q_5 lying between $10^{-3} - 10^3$ times the gas kinetic value, we have, respectively,

$$[O_2 C^3\Sigma] \geq 5 \times 10^7 - 5 \times 10^4/\text{c.c.}$$

for the necessary concentration of $O_2(C^3\Sigma)$ to maintain the excitation and emission of the green line. To show that such concentrations of $O_2(C^3\Sigma)$ are not impossible, we have only to remember that there is a high concentration of $O(^3P)$ for the production of $O_2(C^3\Sigma)$ by the process Q_4 . If there are some 10^{10} $O(^3P)$ atoms per c.c. in the upper atmosphere just after sunset, and if the probability of radiative recombination Q_4 is of the order of 10^{-6} per collision, then the $O_2(C^3\Sigma)$ are produced by Q_4 at a rate of $\sim 10^4/\text{sec. c.c.}$ On assuming a high metastability of the $O_2(C^3\Sigma)$, it will take some 10 minutes to build up a concentration of $O_2(C^3\Sigma)$ of the order $10^6/\text{c.c.}$ which is of the correct order of magnitude to account for the

¹⁷ E. W. Hewson, *Rev. Mod. Phys.*, 1937, **9**, 420.

¹⁸ Lord Rayleigh, *Proc. Roy. Soc.*, 1930, **A 129**, 458.

¹⁹ E. U. Condon, *Astrophys. Jour.*, 1934, **79**, 217.

maintenance of the green line.* This building up of the concentration of $O_2(C^3\Sigma)$ by the process Q_4 may be responsible for the observed slight rise of the intensity of the green line towards midnight.^{3, 4} The slight decline in the intensity of the line in the latter part of the night⁴ may be due to the gradual depletion of the oxygen atoms through the various recombination processes, three-body as well as radiative.

Neglecting the recombination processes compared with the other collisions, we have for the rate of change of the concentration of $O(^1S)$

$$\begin{aligned} \frac{d[O^1S]}{dt} = & Q_5 [O_2 C^3\Sigma]^2 + Q_{19} [N^2D] [O^1D] - \\ & \{A_{green} + A_{trans} + (Q_9 + Q'_9) [N_2 A^3\Sigma] + Q_{15} [N_2^+ X^2\Sigma] \\ & + Q_{21} [Na^2S]\} [O^1S] \end{aligned} \quad (10)$$

where A_{trans} is the probability of the trans-auroral transition $^1S \rightarrow ^3P$ in OI and is $0.18/\text{sec}$.¹⁹ This trans-auroral line is not observed in the night sky or the aurora since it lies just beyond the limit of transparency of the atmosphere. Now for the green line to appear, it is necessary that the rate of quenching by the various processes in (10) be not very large compared with the rate of emission of the line, *i.e.*,

$$A_{green} \ll (Q_9 + Q'_9) [N_2 A^3\Sigma] + Q_{21} [Na^2S] + Q_{15} [N_2^+ X^2\Sigma].$$

In the night sky where the negative bands of N_2^+ are either not present or extremely weak, the last term can be neglected. A knowledge of the cross-sections of Q'_9 and Q_{21} will enable us to set an upper limit to the concentrations of $N_2(A^3\Sigma)$ and sodium atoms. Thus assuming the cross-section for Q'_9 to lie between 10^{-2} and 10^2 times the gas kinetic value, one obtains for $(N_2 A^3\Sigma)$ an upper limit of 10^{13} and $10^9/\text{c.c.}$ respectively. The actual concentration of $N_2(A^3\Sigma)$, especially in the layer where the dissociation of O_2 but not that of N_2 is maximum, is probably very much smaller than

* On taking into account the loss of $O_2(C^3\Sigma)$ through the emission of the Herzberg bands $O_2(C^3\Sigma) \rightarrow O_2(X^1\Sigma)$ and the processes Q_5 , Q'_5 , Q_{12} , Q'_{12} , the rise of the concentration of $O_2(C^3\Sigma)$ will be given by the equation

$$\frac{d[O_2 C^3\Sigma]}{dt} = k - \alpha [O_2 C^3\Sigma] - \beta [O_2 C^3\Sigma]^2$$

where k stands for the constant rate of production by the process Q_4 , α represents the combined result of the processes $O_2(C^3\Sigma) \rightarrow O_2(X^1\Sigma)$, Q_{12} , and Q'_{12} and β the result of Q_5 and Q'_5 . From this one obtains

$$2\beta [O_2 C^3\Sigma] = -\alpha + B \frac{1 - Ae^{-\alpha t}}{1 + Ae^{-\alpha t}},$$

where $B = \sqrt{4k\beta + \alpha^2}$ and $A = (B - \alpha)/(B + \alpha)$. It is seen that the concentration of $O_2(C^3\Sigma)$ will tend to a constant value $(B - \alpha)/2\beta$ after a time t depending on the values of k , α and β .

$10^9/\text{c.c.}$ (see discussion on $[\text{O}_2\text{C } ^3\Sigma]$ above, which are formed by processes analogous to those for $\text{N}_2(\text{A } ^3\Sigma)$).

(B) *Red (OI) lines:* $^1\text{D}_2 \rightarrow ^3\text{P}_{1,2}$

As emphasized in the summary in the introduction, the red (OI) lines of the night sky differ from the green line in their diurnal intensity variations. The O (^1S) atoms in the night sky are probably produced by the process Q_5 . The O (^1D) atoms are, in addition to the analogous but less probable process Q_5' and the result of the emission of the green line, now produced by the process Q_{18} which now assumes greater importance than Q_{19} for the excitation of ^1S , since the initial rate of production of O (^1D) by the process Q_{18} may now be very large on account of the large concentrations of O (^3P) and N (^2D). Assuming as before that immediately after sunset, there are some 10^{10} O (^3P) and some 10^6 N (^2D) atoms per c.c.,²⁰ if the cross-section of Q_{18} is taken to be of the order 10^{-2} times the gas kinetic value, the process Q_{18} will then produce O (^1D) at the rate of some $10^4/\text{sec. c.c.}$ This is amply sufficient to account for the observed intensity of the red lines. With the depletion of the N (^2D) by this and other processes, this rate of production of O (^1D) would have decreased rapidly after sunset had it not been for the replenishment of O (^1D) by the process Q_5' and the result of the emission of the green line. The result is a more gradual decrease in $[\text{O } ^1\text{D}]$ in the early part of the night, followed by a more or less steady value when the rate of depletion by the various processes in equation (11) becomes equal to the rate of replenishment. This may explain the observed fact that the red lines have the greatest intensity immediately after sunset.⁴ The different behaviour of the intensity variations of the green and the red lines is thus due to the different mechanisms for the production of the O (^1S) and O (^1D).

The rate of change of (O ^1D) is, again on neglecting recombinations,

$$\begin{aligned} \frac{d[\text{O } ^1\text{D}]}{dt} = & 2\text{Q}_5' [\text{O}_2\text{C } ^3\Sigma]^2 + \text{Q}_{18} [\text{O } ^3\text{P}] [\text{N } ^2\text{D}] + \text{A}_{\text{green}} [\text{O } ^1\text{S}] - \\ & \{ \text{A}_{\text{red}} + \text{Q}_8 [\text{N}_2\text{A } ^3\Sigma] + \text{Q}_{16} [\text{O}_2\text{X } ^3\Sigma] + \text{Q}_{19} [\text{N } ^2\text{D}] \\ & + \text{Q}_{22} [\text{Na } ^2\text{S}] \} [\text{O } ^1\text{D}] \end{aligned} \quad (11)$$

where the transition probabilities A_{red} are 2.5×10^{-3} and 7.5×10^{-3} per second for the lines $^1\text{D}_2 \rightarrow ^3\text{P}_1$ and $^1\text{D}_2 \rightarrow ^3\text{P}_2$ respectively.¹⁹ The red lines

²⁰ The value $10^6/\text{c.c.}$ for $[\text{N } ^2\text{D}]$ is based on the following estimates: Kaplan pointed out the possible appearance of the lines $^2\text{D} \rightarrow ^4\text{S}$ in NI with about 1/50 the intensity of the green [OI] line in Babcock's spectrum of the night sky (see C below). Since the lifetime of N (^2D) is of the order 10^5 second, this requires that there be at least some 10^6 N (^1D) per c.c. to account for the observed intensity.

are here quenched by the processes Q_8 and Q_{16} . As Q_8 and Q_{16} are probably of the same order of magnitude and as the concentration of the oxygen molecule in the normal state is certainly larger than that of the $N_2(A\ ^3\Sigma)$ by some powers of 10, we need only consider the quenching by Q_{16} . The condition for the red lined to appear is hence

$$A_{red} \ll Q_{16} [O_2 X\ ^3\Sigma].$$

Assuming that the cross-section for Q_{16} is 10^{-2} to 10^2 times the gas kinetic value, one finds that for the red lines to appear, $(O_2 X\ ^3\Sigma)$ must not be very much greater than 10^{10} and $10^6/\text{c.c.}$ respectively. Even the value $10^{10}/\text{c.c.}$ is too low for the E layer where the concentration of O_2 is probably of the order $10^{11} - 10^{12}/\text{c.c.}$ The above condition is more readily satisfied in the higher altitudes. This may be connected with the observed enhancement of the red lines in the sunlit auroræ⁶ which are situated in very much higher altitudes (300 — 800 km.) than the ordinary auroræ (100 km), although the enhancement may also be due to the production of $O(^1D)$ by the photo-dissociation process (3).

Finally we may remark in passing that the great difference in the relative intensity of the green and the red lines in the night sky and in the nebulæ is not a matter of the difference in the gas pressures in the two cases alone. From equations (10) and (11), it is seen that were it not for the quenching collisions, the red lines would have been more intense than the green since any excitation of $O(^1S)$ by Q_5 would contribute to the intensity of the red lines on emission of the green line. That the red lines are weaker than the green is probably due to the more effective quenching of the former by Q_{16} (exciting at the same time the A, B, α bands of oxygen) than that of the latter by the process $O_2(X\ ^3\Sigma) + O(^1S) \rightarrow O_2(A\ ^1\Sigma) + O(^1D)$, since here the spin rule is violated. On the other hand, the extremely low pressure in the nebulæ renders quenching collisions of any kind unimportant, and the intensities of the green and the red lines are determined essentially by the relative frequencies of excitations of 1S and 1D . That the red lines are far more intense than the green line in the nebulæ is to be explained by the predominance of electrons having energies enough to excite 1D but not 1S . In fact, from the relative intensities of the red and the green lines and the theoretical excitation cross-sections of these states by electron impact, it has been possible to obtain very reasonable values for the temperatures of the nebulæ.²¹

²¹ D. H. Menzel, L. H. Aller and M. H. Hebb, *Astrophys. Jour.*, 1941, 93, 230.

(C) *Forbidden lines of [NI] $^2D \rightarrow ^4S$*

The situation with the forbidden lines of NI can be expected to be similar to that with OI. The lines $^2P \rightarrow ^2D$ have transition probabilities of the order 1/sec.; they lie in the infra-red 1.04μ and hence have not been observed. The lines $^2D \rightarrow ^4S$ have the small transition probabilities of the order 10^{-5} /sec. Kaplan has recently succeeded in observing both the $^2D \rightarrow ^4S$ and the $^2P \rightarrow ^4S$ lines in afterglows in nitrogen under moderately high pressure, and has pointed out the probable appearance of $^2D \rightarrow ^4S$ in Babcock's spectrogram of the night sky with an intensity about 1/50 that of the green [OI] line.²² If this identification is correct, we may consider the equations

$$\frac{d[N \ ^2P]}{dt} = Q_6'' [N_2 A \ ^3\Sigma]^2 - \{A(^2P \rightarrow ^2D) + A(^2P \rightarrow ^4S) + (Q_9 + Q_9') [N_2 A \ ^3\Sigma] + Q_{14} [N_2 + X \ ^2\Sigma]\} [N \ ^2P], \quad (12)$$

$$\begin{aligned} \frac{d[N \ ^2D]}{dt} = & 2 Q_6' [N_2 A \ ^3\Sigma]^2 + A(^2P \rightarrow ^2D) [N \ ^2P] - \{A(^2D \rightarrow ^4S) + \\ & (Q_{10} + Q_{10}') [N_2 A \ ^3\Sigma] + Q_{17} [O_2 X \ ^3\Sigma] + Q_{18} [O \ ^3P] + Q_{19} [O \ ^1D] + \\ & Q_{20} [Na \ ^2S]\} [N \ ^2D], \quad (13) \end{aligned}$$

in which recombination processes have again been omitted. The initial concentrations of $N(^2P)$ and $N(^2D)$ immediately after sunset may be very large, especially at the level where the dissociation of N_2 is most intense. The large value of $A(^2P \rightarrow ^2D)$, however, reduced $(N \ ^2P)$ rapidly to a low value so that the more or less steady but small concentration during the night is determined by the rate of the process Q_6'' , which may be much smaller than the corresponding process Q_5 in the case of the excitation of $O(^1S)$ on account of the very much larger energy discrepancy (1.3 volt vs. 0.12 volt). On the other hand, the small value $A(^2D \rightarrow ^4S)$ can be consistent with a considerably higher value of $[N \ ^2D]$. This may be the reason why the nebular $^2D \rightarrow ^4S$ can be observed while the trans-auroral $^2P \rightarrow ^4S$ at 3466 Å with a much greater transition probability cannot.²³

(D) *Negative bands of $N_2^+ N_2^+ : (B \ ^3\Sigma) \rightarrow N_2^+ (X \ ^2\Sigma)$*

Once we have assumed the generation of N_2^+ by solar radiations by such process as (7), it is not necessary to assume other modes of generation during the night when one remembers the low rate of loss of N_2^+ by recombination processes. In fact, that the N_2^+ bands are greatly enhanced

²² J. Kaplan, *Phys. Rev.*, 1939, **56**, 858 ; 1940, **57**, 249.

²³ R. Bernard, *Phys. Rev.*, 1939, **55**, 511 ; Elvey, Swings and Linke, *Astrophys. Jour.*, 1941 **93**, 337.

relative to the green [OI] line in sunlit auroræ²⁴ and that the N_2^+ bands in the night sky increase in intensity when the last trace of sun light touches the uppermost part of the atmosphere in the evening and when the first trace of sun light reaches the top of the atmosphere at the dawn²⁵ are consistent with the view that the N_2^+ are produced by solar radiations. It is true that the very much greater intensity of the N_2^+ bands in the auroræ than in the night sky cannot be explained without additional hypotheses about the auroræ. But granting a higher concentration of N_2^+ in the aurora, one can then understand why the N_2^+ bands are strong and the Vegard-Kaplan bands are weak in the aurora and conversely in the night sky; for the N_2^+ bands excited by the process Q_{13} are at the expense of the metastable $N_2(A^3\Sigma)$, thus quenching the Vegard-Kaplan bands (see below on Vegard-Kaplan bands).

As summarized in the introduction, the strongest N_2^+ bands in the aurora and the night sky are the $v' - v'' = 0 - 0; 0 - 1; 0 - 2; 1 - 2; 1 - 3; 2 - 3$ bands. The strong enhancement of transitions from $v' = 0, 1, 2$ may be ascribed to the excitation processes Q_{14} and Q_{15} . The enhancement of the N_2^+ bands in sunlit aurora and sunlit atmosphere is also consistent with this view since the concentrations of $N(^2P)$ and $O(^1S)$ generated by sun light by the processes (1), (2), (3) and possibly also (6) and (8) will be high in the sunlit regions. The transition $v' = 11 \rightarrow v'' = 13$ has a wavelength 4233.5 Å for the band centre so that its head falls just on top of the 4236 (1 \rightarrow 2) bands. Also the $v' = 12 \rightarrow v'' = 13$ band has the wavelength 3915 and may contribute partly to the great intensity of the 3914 (0 \rightarrow 0) band. This may perhaps account for the excitation of the N_2^+ bands by $N_2(A^3\Sigma)$.

(E) *Second positive bands: $N_2(C^3II) \rightarrow N_2(B^3II)$*

The only plausible processes for the excitation of the second positive system of N_2 are Q_6 and Q_{12} . The equation for $[N_2(C^3II)]$ is

$$\frac{d[N_2C^3II]}{dt} = Q_6 [N_2A^3\Sigma]^2 + Q_{12} [N_2A^3\Sigma] [O_2C^3\Sigma] - A_{2nd} [N_2C^3II] = 0. \quad (14)$$

Here no quenching collisions need be considered. The process Q_{12} will be able to excite $v' = 0$ of C^3II only when the $N_2(A^3\Sigma)$ is initially in a state $v = 1$ (see end of G) below, while the 10550 cm^{-1} energy available in the process Q_6 can either all go into the excitation of $N_2(B^3II)$, or be divided

²⁴ C. Störmer, *Zeits. f. Geophys.*, 1929, 5, 185.

²⁵ V. M. Slipher, *Monthly Notices, R.A.S.*, 1933, 93, 657.

between the vibrational motions of the two resulting molecules. In the first case, the bands from $v' = 0$ will be enhanced; in the second case, all bands up to $v' = 5$ can be excited, with perhaps some enhancement of $v' = 1, 2$. As seen from the summary in the introduction, these are in general agreement with the observed facts.

(F) *First positive bands*: $N_2(B\ ^3\Pi) \rightarrow N_2(A\ ^3\Sigma)$

The first positive bands are the characteristic feature of the night sky, the aurora and the afterglow in nitrogen. In the afterglow, Kaplan has succeeded in exciting the $v' - v'' = 3$ sequence with intensity maxima corresponding to $v' = 10$ and $v' = 6$. These enhancements have been explained as due to the processes Q_9 and Q_{10} . In the aurora, Vegard observed the bands $v' = 10 \rightarrow v'' = 7$ at 6323 Å. and $v' = 7 \rightarrow v'' = 6$ at 7880 Å. These seem to indicate the processes Q_9 and Q_{10} . In the night sky, bands from very high vibrational levels such as $v' = 15, 16$ have been found. These excitations are furnished by the processes Q_7, Q_8 and Q_{12}' . These together with Q_9 and Q_{10} may account for the excitation of bands from $v' = 4$ to $v' = 15$ or higher observed in the night sky by Cabannes and Elvey, Swings and Linke.^{3, 4}

(G) *Vegard-Kaplan bands*²⁶ $N_2: (A\ ^3\Sigma) \rightarrow N_2(X\ ^1\Sigma)$

The equation for the rate of change of $[N_2A\ ^3\Sigma]$ is

$$\begin{aligned} \frac{d [N_2A\ ^3\Sigma]}{dt} = & Q_1 [N\ ^4S]^2 [X] + Q_3 [N\ ^4S]^2 - \\ & \{A_{v,K} + (Q_6 + 2 Q_6' + 2 Q_6'') [N_2A\ ^3\Sigma] + Q_7' [O\ ^1S] + Q_9' [N\ ^2P] + \\ & Q_{10} [N\ ^2D] + Q_{11} [O_2X\ ^3\Sigma] + Q_{13} [N_2^+X\ ^2\Sigma]\} [N_2A\ ^3\Sigma] \end{aligned}$$

As the Vegard-Kaplan bands arise from transitions violating the selection rule for the multiplicity, they have small transition probabilities. Accordingly they will be emitted only if

$$A_{v,K} \ll \{Q_6 + 2 Q_6' + 2 Q_6''\} [N_2A\ ^3\Sigma] + Q_7' [O\ ^1S] + Q_9' [N\ ^2P] + Q_{10}' [N\ ^2D] + Q_{11} [O_2X\ ^3\Sigma] + Q_{13} [N_2^+X\ ^2\Sigma]. \quad (15)$$

Thus the emission of these bands requires a low $[N_2^+X\ ^2\Sigma]$ and of course the absence of ultraviolet radiations that may destroy the $N_2(A\ ^3\Sigma)$ by

²⁶ This "complementary" nature of the negative bands of N_2^+ and the Vegard-Kaplan bands is true not only of the aurora and the night sky, but seems to be true also in the discharge tube. In the afterglow produced by a feeble discharge, Kaplan (*Pub. Astron. Soc. Pacif.*, 1935, **47**, 257), found that the Vegard-Kaplan bands are enhanced relative to the second positive bands while the N_2^+ bands are absent. On the other hand, when the N_2^+ bands are strong, the Vegard-Kaplan bands are not found (Kaplan, *Phys. Rev.*, 1932, **42**, 807).

the processes (6) and (7). This is in agreement with the fact that in the sunlit aurora where the N_2^+ bands are strong and hence $[N_2^+X^2\Sigma]$ high, the Vegard-Kaplan bands are weak, while in the night sky where the N_2^+ bands are weak, the Vegard-Kaplan bands are strong.

It is observed that the blue radiations of the night sky reach a maximum intensity immediately after midnight,²⁷ like the green [OI] line. Now the strongest radiations in the blue region are the 4171 and 4425 bands of the Vegard-Kaplan system. A rise of intensity of these bands in the first part of the night may be due to the same cause as that for the green line, namely, the building up of the concentration of the metastable N_2 ($A^3\Sigma$) by the processes Q_1 and Q_3 . Its decline in the second part of the night can be ascribed to the gradual depletion of the N atoms.

In the night sky, Vegard-Kaplan bands from all levels v' up to 7 are observed, the bands from $v' = 2, 3, 4$ being particularly enhanced. It is of course not possible to say anything about the populations of the different levels of the N_2 ($A^3\Sigma$) resulting from the radiative process Q_3 . But those produced by the process Q_1 may be in any state v' up to 7 since the energy available in the process is 1.2 volt. There may be a preponderance of levels $v' = 2, 3, 4$ corresponding to the division of this energy between the two resulting molecules N_2 ($A^3\Sigma$) and N_2 ($X^1\Sigma$). Also the large number of N_2 ($A^3\Sigma$) molecules resulting from the emission of the first positive bands $v' = 6, 7 \rightarrow v'' = 3, 4$ would enhance the Vegard-Kaplan bands from $v' = 3, 4$.

In discussing the enhancement of certain bands in a system involving allowed transitions, it is necessary only to consider the levels excited with close resonance since the lifetimes of these states are so short that a redistribution by collisions can be neglected. With the Vegard-Kaplan bands, on account of the long lifetime of the metastable state $A^3\Sigma$, it is necessary to consider the effect of collisions between the N_2 ($A^3\Sigma$) molecules and other particles. It is known, however, both experimentally and theoretically that the probability of energy transfer between the vibrational motion of a molecule and the translational motion of an atom or a molecule is very small, of the order $10^{-7} - 10^{-6}$ per collision.²⁸ As the collision frequency of an atom or a molecule with other molecules is of the order 10^3 per second at the pressure of the E layer, it is clear that de-excitation of vibrational excitation by collisions is unimportant. This persistence of vibrational excitation accounts for the emission of Vegard-Kaplan bands from rather high levels v .

²⁷ N. E. Bradbury and W. T. Sumerlin, *Phys. Rev.*, 1940, **57**, 249.

²⁸ Cf. Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press, 1933, p. 249.

(H) *Lyman-Birge-Hopfield Bands*: $N_2(a^1\Pi) \rightarrow N_2(X^1\Sigma)$

The existence of these bands, especially those from $v' = 0$ to $v'' = 19 - 23$, has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.⁴ It is suggested here that this system of bands is excited from the metastable $N_2(A^3\Sigma)$ by the metastable $N(^2D)$, $N(^2P)$ and $O(^1S)$ by the processes Q_{10}' , Q_9' , Q_7' respectively. While $N(^2P)$ and $O(^1S)$ can excite the vibrational levels $v' = 6$ and 9 respectively, $N(^2D)$ excites $v' = 0$ with almost exact resonance (energy discrepancy $\simeq 1/400$ of a volt). This may account for the enhancement of the bands $3378 (0 \rightarrow 19)$, $3834 (0 \rightarrow 21)$, $4420 (0 \rightarrow 23)$. The possible appearance of bands from $v' = 10$ or higher may arise from excitations by $O(^1S)$ of $N_2(A^3\Sigma)$ initially in the vibrational levels $v = 1, 2$ or 3 . That this is possible is seen from the foregoing discussion of the persistence of vibrational excitation.

The equation for the rate of change of $[N_2 a^1\Pi]$ is

$$\frac{d[N_2 a^1\Pi]}{dt} = \{Q_7' [O^1S] + Q_9' [N^2P] + Q_{10}' [N^2D]\} [N_2 A^3\Sigma] - A_{LBH} [N_2 a^1\Pi] = 0. \quad (16)$$

Again no quenching collisions need be considered here.

(I) *Atmospheric bands of O_2* : $(A^1\Sigma) \rightarrow O_2(X^3\Sigma)$

If the existence of the "A", "B", " α ", " α' ", " α'' " bands of O_2 corresponding to the transitions $0 \rightarrow 0$, $1 \rightarrow 0$, $2 \rightarrow 0$, $3 \rightarrow 0$, $4 \rightarrow 0$ respectively in the night sky is established, then a mechanism for the excitation of the first three is provided by the process Q_{16} and one for the last two by Q_{17} . These processes are responsible for the partial quenching of the "nebular" lines in [OI] and [NI] respectively.

(J) *Schumann-Runge bands of O_2* : $[B^3\Sigma] \rightarrow O_2(X^3\Sigma)$

The observations of Dufay, Gauzit, Elvey, Swings and Linke suggest very strongly the presence of the Schumann-Runge bands in the night sky, especially those from the levels $v' = 0$ and 1 . A mechanism for the excitation of these bands is provided by the process Q_{11} whose cross-section may not be small since the energy discrepancy for excitation of $v' = 0$ is only $1/20$ of a volt.

(K) *Na lines*: $^2S - ^2P$

The yellow lines of sodium have been observed in the night sky and various aspects of the problem concerning it have been discussed by a number of authors. Chapman suggested the process Q_{22} for the excitation mechanism and accounted for the energy deficiency of 0.14 volt by means

of the kinetic energy of the particles.²⁹ The fraction, however, of atoms having this kinetic energy is very small unless the temperature of the atmosphere has a value above 1000° K., for which there does not seem to be very strong evidence (see foot-note 30 below). On the other hand, the process Q_{20} is energetically more probable, and on account of the smaller transition probabilities $A(^2D \rightarrow ^4S)$ than those for the red [OI] lines, the concentration of N(2D) may be greater than that of O(1D). The process Q_{21} has an even higher cross-section since the resonance is closer and the spin rule is satisfied. This may make up for the low concentration of O(1S) and has to be taken into account in assessing the relative importance of the various processes for the excitation of the Na lines. More information concerning the variations of the intensity of the Na lines with time and altitude is necessary for a proper understanding of the problem of atmospheric sodium.

(L) *Water vapour bands*

According to Cabannes, the water vapour bands at 0.59μ , 0.65μ , 0.698μ , 0.72μ corresponding to $4 \nu_1 + \nu_3$, $3 \nu_1 + \nu_2 + \nu_3$, $\nu_1 + 3 \nu_3$, $3 \nu_1 + \nu_3$ respectively are present in the spectrum of the night sky, and possibly also in the aurora.³ These bands, if their existence is established, are interesting in that they differ from all the other radiations in being pure vibration-rotational bands. The most effective modes of excitation would be a collision of the first kind with another atom or molecule, or a collision of the second kind with a molecule in a vibrationally excited state. The probability of the first collision is extremely small, and the fraction of particles having a kinetic energy of the order of 1 volt must be exceedingly small. On the other hand, molecules in highly vibrationally excited states [such as $v=13, 14, 15$ in $N_2(X^1\Sigma)$ as the result of the Vegard-Kaplan transitions] may be fairly abundant, and it is possible that these molecules are responsible for the excitation of the water vapour bands by a resonance process.

The existence of these high combination, and hence weak, water vapour bands in the night sky would indicate appreciable concentration of water vapour in the upper atmosphere. As water vapour plays the most important part in the problem of radiative equilibrium of the earth's atmosphere, it would be desirable to have some measurements of the absolute intensities

²⁹ S. Chapman, *Astrophys. Jour.*, 1939, **90**, 309. The mechanism $NaO + O \rightarrow Na + O_2$ suggested there for the maintenance of free Na atoms in the presence of oxygen has to be considered not only from the point of view of energies, but also together with the fact that the process involves an activation energy approximately equal to the dissociation energy of NaO. At the temperature of the upper atmosphere, such a process will be exceedingly improbable.

and some theoretical estimates of the transition probabilities of these bands so that one may estimate the concentration of water vapour, and hence the temperature, of the upper atmosphere.³⁰

(M) *Other radiations*

It seems to be generally agreed that in the spectra of the night sky and the aurora, there are no atomic lines other than the lines of [OI], and possibly the $^2D \rightarrow ^4S$ of [NI].³¹ The absence of the atomic lines of N, O as well as H and other rare gases is now understandable since the energies available for excitation in the metastable atoms and molecules of nitrogen and oxygen do not exceed 6.1 volts. In fact, the strong point of the proposed mechanisms here is that they provide a reasonable process for each of the radiations observed and at the same time allow satisfactorily for the absence of others that are not observed.

Concerning the possible presence of bands from such molecules as NO, NH, CH and CN, the observational material is still too meagre to warrant any discussion. In any case, the bands, if they are definitely confirmed, are so weak and so scanty that these molecules must be very rare in the upper atmosphere. The absence or scarcity of NO alone perhaps

³⁰ It seems that no accurate knowledge concerning the temperature of the upper atmosphere of the earth is available. Vegard (quoted in Rosseland's *Theoretical Astrophysics*, Oxford Univ. Press, 1936, pp. 234-37) has estimated the temperature of the aurora from the intensity distribution in the unresolved 4278 Å. band of N_2^+ and found a value 70° C. This can only be a rough estimate on account of the low dispersion of the spectrum. [The formula on p. 234 for the intensity of a rotational line in a band, namely, $I(j \rightarrow j+1) \propto (2j+1) \exp. (-E_j/kT)$, is slightly in error as it does not take into account the factor depending on the transition probability of the line. The correct expression is $(j+1) \exp. (-E_j/kT)$]. More recently, from the R branch of the 4278 band, Vegard and Tonsberg, *Geofys. Pub.*, 1938, 12, 3, obtain a temperature of -35° C. In any case, the temperature so determined will represent the temperature of the atmosphere only if the excitation process does not greatly change the distribution in the rotational states, for example, if the bands are excited by electron impact. On the other hand, if the bands are excited by collisions of the second kind with heavy particles, the temperature parameter determined from the intensity distribution in a band may differ from the thermal temperature in a way depending on the probability of energy transfer to and from the rotational motion in such collisions.

On the basis of the theory of intensities of electronic transitions and the intensity distribution in the negative bands of N_2^+ and the positive bands of N_2 , Rosseland and Steensholt (quoted in Rosseland's book, p. 244) have also calculated the temperature of the aurora and found values of the order 2000°-3000° K. As emphasized by Rosseland, these values must not be taken to mean the temperature of the atmosphere since the bands are assumed to have been excited by swift particles not in thermal equilibrium with the atmosphere. On our view here, the bands are excited by collisions of the second kind. The intensity distribution in a band system depends then only on the resonance mechanism and has nothing to do with the temperature of the atmosphere at all.

³¹ For the aurora spectrum, M. Nicolet, *Ann. d'Astrophys.*, 1938, 1, 381; for the night sky, Elvey, Swings and Linke, *Astrophys. J.*, 1941, 93, 337.

needs some consideration, in view of the abundance of the N and O atoms. This is probably because of the fact that the layers of maximum dissociation of the nitrogen and the oxygen molecules, and hence the layers of maximum concentration of the N and O atoms, are different. Thus while a concentration of O atoms of $10^{10}/\text{c.c.}$ will lead to a recombination into O_2 at a rate of $10^4/\text{sec. c.c.}$, the presence of N atoms at the same layer with a concentration $10^6/\text{c.c.}$ will lead to the formation of only 1 NO per sec. per c.c.

Concluding Remarks

To sum up, then, it is seen from the present theory that the various emission processes take place at the expense of the energies of excitation of the metastable atoms and molecules of N and O, and these metastable atoms and molecules are constantly replenished by the recombinations of the atoms generated by photo-dissociation during the day. It is interesting to note that the various processes do not all proceed in one direction alone, with a consequent rapid depletion of the metastable atoms or molecules. Rather many of these processes form cycles so that continual excitation and emission of the various radiations are possible. The overall result of all the processes is, of course, the recombinations of the atoms into molecules. For example, from equations (12), (13), (15), (16) and the following ones

$$\begin{aligned} \frac{d[\text{N}^4\text{S}]}{dt} = & \{Q_6'' [\text{N}_2\text{A } ^3\Sigma] + (Q_9 + Q_9') [\text{N}^2\text{P}] + (Q_{10} + Q_{10}') [\text{N } ^2\text{D}]\} [\text{N}_2\text{A } ^3\Sigma] \\ & + \{Q_{17} [\text{O}_2\text{X } ^3\Sigma] + Q_{18} [\text{O } ^3\text{P}] + Q_{19} (\text{O } ^1\text{D}) + \text{A } (^2\text{D} \rightarrow ^4\text{S})\} [\text{N } ^2\text{D}] \\ & + Q_{14} [\text{N}_2^+\text{X } ^2\Sigma] [\text{N } ^2\text{P}] - 2(Q_1 [\text{X}] + Q_3) [\text{N}^4\text{S}]^2, \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{d[\text{N}_2\text{X } ^1\Sigma]}{dt} = & \{(Q_6 + Q_6' + Q_6'') [\text{N}_2\text{A } ^3\Sigma] + Q_{13} [\text{N}_2^+\text{X } ^2\Sigma] + \text{A}_{\text{v.k.}}\} [\text{N}_2\text{A } ^3\Sigma], \\ & + \text{A}_{\text{LBH}} [\text{N}_2\alpha ^1\Pi], \end{aligned} \quad (18)$$

we have, as we expect,

$$\frac{d}{dt} \{[\text{N}^4\text{S}] + [\text{N } ^2\text{D}] + [\text{N } ^2\text{P}] + 2[\text{N}_2\text{X } ^1\Sigma] + 2[\text{N}_2\text{A } ^3\Sigma]\} = 0. \quad (19)$$

As $\frac{d}{dt} [\text{N}_2\text{X } ^3\Sigma]$ must be positive since in the absence of sunlight no collision process can lift the N_2 molecule from the normal state or dissociate it, and as $\frac{d}{dt} [\text{N}_2\text{A } ^3\Sigma]$ must be $\simeq 0$ in the steady (or very slowly varying) state during the night when the intensity of the Vegard-Kaplan bands does not vary greatly, it follows that

$$\frac{d}{dt} \{[\text{N}^4\text{S}] + [\text{N } ^2\text{D}] + [\text{N } ^2\text{P}]\} < 0,$$

i.e., the net result of the various processes is a steady decrease in the concentrations of the atoms. Entirely similar result holds for the processes

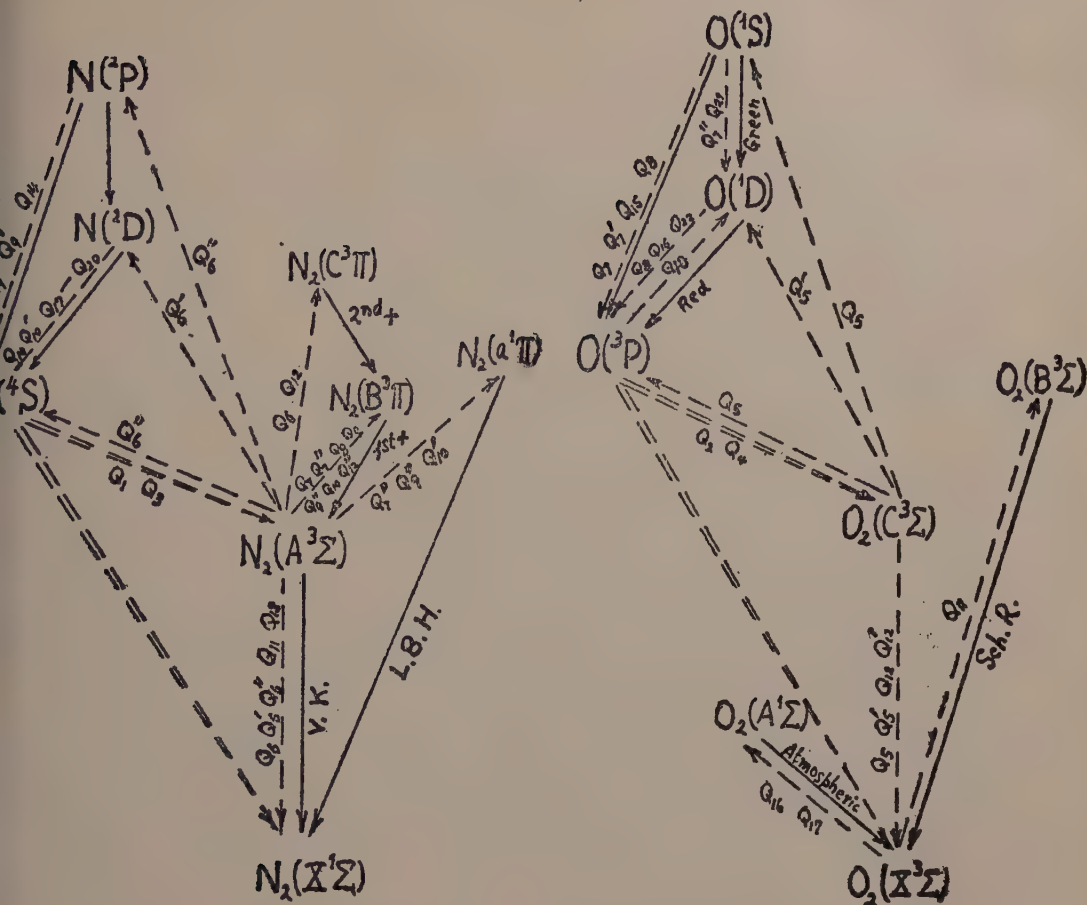


FIG. 2. Excitation processes in the night sky and the aurora
Solid lines indicate radiative transitions ; dashed lines represent excitation collisions

involving the oxygen atoms and molecules. The O atoms disappear either through the radiative processes of the type Q_4 or through three-body processes of the type Q_2 , followed by processes Q_5 , Q_{12} and others, ending eventually in the normal state $O_2(X^3\Sigma)$. The various processes and their interrelations are rendered clear by the diagrams in Figs. 1 and 2.

Finally we need only add that the rates of the various processes of excitation and radiation depend either directly or indirectly on the rates of supply of the metastable $N_2(A^3\Sigma)$ and $O_2(C^3\Sigma)$ molecules, which in turn depend on the rates of recombination of the atoms. As these recombinations are the bottle-neck of the various processes, we need only consider them in order to see if the supply of atoms at sunset will last through the

night. That they will last is seen from our estimate of the rate of recombination of the O atoms in connection with the discussion of the green [OI] line.

Summary

It is shown that the main features in the selective emission spectra of the night sky and the aurora, namely, the forbidden [OI] lines, the various systems of bands of N_2^+ and N_2 and O_2 , and in particular, the enhancement of certain lines and bands relative to others and the diurnal variations of the intensity of certain lines in the night sky, can be satisfactorily explained on the view that all the excitation and quenching processes in the upper atmosphere are collisions of the second kind, of the resonance type, between the metastable atoms and molecules of nitrogen and oxygen. The metastable atoms are generated in the night by collisions between the metastable molecules; the latter are in turn formed by the recombinations of the normal atoms which are produced by photo-dissociation of the molecules during the day. A strong argument for the theory is that, not only the observed radiations are provided with reasonable excitation processes, but the absence of other atomic lines N, O, H and the rare gases is automatically accounted for by the maximum energy available for the excitations in these metastables, which is only 6.1 volts (the energy of $N_2 [A^3\Sigma]$). It is suggested that these processes in Table II are the microscopic processes responsible for the observed spectra, while such large-scale features as the shapes of the auroræ and seasonal variations in the intensities, etc., may have to be explained by further hypotheses.

OPTICAL THEORY OF CHROMATIC EMULSIONS AND OF THE CHRISTIANSEN EXPERIMENT

BY G. N. RAMACHANDRAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received July 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

WHILE engaged upon some determinations of the refractive index of transparent powders by the method of immersing them in liquid mixtures of the same refractive index, Christiansen (1884) observed some very remarkable and interesting colour effects. If white light was employed, the transmitted light was highly coloured, the colour corresponding to the particular wave-length for which the two substances have the same refractive index. Lord Rayleigh (1885) repeated these experiments, and found that the transmitted spectrum was remarkably narrow. The subject was investigated in detail by Sethi (1921), who studied the effect of the size and number of the particles and of the thickness of the medium on the transmitted light, and also the light scattered in other directions. He extended his studies to the colours shown by emulsions of immiscible liquids, whose refractive indices are equal for some wave-length in the visible range. The elegant method of preparing these emulsions in a stable state, discovered by Holmes and Cameron (1922), enabled Sogani (1926) to make a thorough study of the phenomena exhibited by these "chromatic emulsions".

Lord Rayleigh has rightly remarked (1899) that a proper theory of the Christiansen phenomenon must be based on wave-optical ideas. Following the lines suggested by Rayleigh, both Sethi and Sogani have tried to explain, theoretically, the phenomena observed by them. But their method is not comprehensive, since separate theories have to be worked out to explain the transmission colours, and the colours of the light scattered in other directions. In this paper, an attempt is made to explain the whole range of phenomena on a single theory based on the diffraction of light by a transparent sphere, whose refractive index is not appreciably different from that of the surrounding medium. The author (1943 *a*) has already developed such a theory in connection with the study of the transmission of light through a cloud of transparent droplets. As a particular case, the theory

has been used to explain the occurrence of coronæ when a bright object is viewed through thin cloud (1943 *b*).^{*} The application of the theory to the explanation of the properties of chromatic emulsions forms another particular case, not covered by the previous one. The theory is strictly applicable only to spherical particles, and hence only to the case of chromatic emulsions; nevertheless as we shall see in the course of the paper, it suffices to give a good account of the phenomena observed in the Christiansen experiment with particles of arbitrary shape.

2. Intensity and Spectral Nature of the Transmitted Light

If a sphere of radius a , and of refractive index μ , be placed in a medium of refractive index μ_0 , then the amplitude of the wave diffracted in a direction making an angle ϕ with the incident direction can be shown (1943 *a*) to be

$$X = X_1 - X_2, \quad (1)$$

$$\begin{aligned} \text{where } X_1 = & K \sin \chi \int_0^{\pi/2} J_0(\eta \sin \theta) \cos(\xi \cos \theta) \sin \theta \cos \theta d\theta \\ & - K \cos \chi \int_0^{\pi/2} J_0(\eta \sin \theta) \sin(\xi \cos \theta) \sin \theta \cos \theta d\theta, \end{aligned} \quad (2)$$

$$X_2 = K \sin \chi \cdot J_1(\eta)/\eta, \quad (3)$$

$$\xi = 4\pi(\mu - \mu_0)a/\lambda, \quad \eta = 2\pi a\mu_0 \sin(\phi)/\lambda \text{ and } K = 2\pi a^2/\lambda, \quad (4)$$

the incident wave being represented by $\sin \chi$, and λ being its wave-length in vacuum.

In the exact forward direction, however, the effect of the incident wave would also be present. If we denote the amplitude due to the incident wave as X_0 , then that due to the transmitted wave is

$$X' = X_0 + X_1' - X_2' \quad (5)$$

where X_1' and X_2' are the values of X_1 and X_2 when $\phi = 0$. For this case, $\eta = 0$, and the integrals in (2) can be integrated (1943 *a*) giving

$$\begin{aligned} X' = & X_0 + K \sin \chi \left\{ \frac{\cos \xi}{\xi^2} + \frac{\sin \xi}{\xi} - \frac{1}{\xi^2} - \frac{1}{2} \right\} \\ & - K \cos \chi \left\{ \frac{\sin \xi}{\xi^2} - \frac{\cos \xi}{\xi} \right\} \\ = & X_0 - KC_1' \sin \chi - KS' \cos \chi \text{ (say)} \end{aligned} \quad (6)$$

^{*} Hereafter, these papers will be referred to as (1943 *a*) and (1943 *b*) respectively.

where $K = 2\pi a^2/\lambda$. Now, if A be the aperture of the beam, X_0 is evidently $= A \sin(\chi)/\lambda$, so that

$$X' = \frac{A}{\lambda} \sin \chi \left\{ 1 - \frac{2\pi a^2}{A} C_1' \right\} - \frac{A}{\lambda} \cos \chi \left\{ \frac{2\pi a^2}{A} S' \right\}. \quad (7)$$

The above expression applies to a single droplet. Applying the method used in Section 5 of (1943 a), it is easily shown that the attenuation coefficient is

$$b = -4\pi a^2 N C_1' \quad (8)$$

and the refractive index, n , is given by

$$n - \mu_0 = N \lambda a^2 S' \quad (9)$$

where N is the number of droplets per unit volume. Thus, if l be the thickness of the emulsion, then the intensity of the transmitted light is

$$I = I_0 \exp[-bl] = I_0 \exp[-4\pi a^2 N l C_1'], \quad (10)$$

where I_0 is the intensity of the incident light.

The value of C_1' is given by (6). But, in the Christiansen experiment, and in the case of chromatic emulsions, the refractive indices of the two media are the same for some particular wave-length, say λ_0 , and differ at other wave-lengths. The important colour effects, and other phenomena in which we are interested occur in a small range of wave-lengths about λ_0 , where $(\mu - \mu_0)$ has only a very small value. Hence, the range of values of ξ that would be required will be only small, comprising of small positive and negative values. In order to be applicable for this range, C_1' can be expanded in the form of a power series in ξ as

$$C_1' = \xi^2/8 - \xi^4/144 + \dots \quad (11)$$

so that, for small values of ξ , $C_1' = \xi^2/8$. If larger values of ξ occur in any case, expression (6) can be used.

Hence, for small values of ξ ,

$$I_l/I_0 = \exp[-\pi a^2 N l \xi^2/2]. \quad (12)$$

This equation gives the variation of the intensity of the transmitted light with various factors.

Taking first the variation with ξ , it is easily seen that $I_l = I_0$ at $\xi = 0$, and decreases rapidly as ξ^2 increases, the graph connecting I_l and ξ having the shape of the well-known probability curve. Now ξ is a function of both $(\mu - \mu_0)$ and λ . But, the variation of ξ with λ is only a steady one, so that we shall at first neglect this variation, and consider only the effect of changes in the value of $(\mu - \mu_0)$. The effect of the change in the wave-length will be finally discussed.

Substituting the value for ξ , (12) becomes

$$I_t/I_0 = \exp [-8\pi^3 N l (\mu - \mu_0)^2 a^4 / \lambda^2] \quad (13)$$

$$= \exp [-\gamma (\mu - \mu_0)^2] \text{ (say),}$$

where

$$\gamma = 8\pi^3 N l a^4 / \lambda^2. \quad (14)$$

It is now seen that the intensity of the transmitted light is a maximum, being equal to that of the incident light for $\lambda = \lambda_0$. For both smaller and larger wave-lengths, $(\mu - \mu_0)^2$ increases, so that the intensity diminishes. Thus, only a small range of wave-lengths on either side of λ_0 is transmitted.

It is now interesting to examine how the spectral width of this region of transmission is altered by other factors. As an approximate value of the width, one may take it as equal to the range of wave-lengths, within which the intensity falls to a definite fraction (say $1/e$) of the maximum intensity. Then, $I_t/I_0 = e^{-1}$, so that the width is given by the range of wave-lengths for which

$$\gamma (\mu - \mu_0)^2 < 1, \text{ or } |\mu - \mu_0| < 1/\sqrt{\gamma} \quad (15)$$

Hence, the region of transmission narrows with the increase of γ , and *vice versa*. The following results immediately follow from this:

(a) The region of transmission should sharpen with the increase of the thickness, l , of the emulsion and *vice versa*.

(b) As the concentration of the dispersed phase is increased, the value of N is increased, so that the spectrum of the transmitted light must become narrower, and *vice versa*.

(c) An emulsion containing fine particles must transmit a wider region of the spectrum than one containing coarse droplets, since a is smaller.

(d) The more widely different are the relative dispersive powers of the two media, the narrower is the spectral region transmitted. This is so, since the range of values of λ within which $(\mu - \mu_0)^2$ becomes equal to $1/\gamma$ is small, if the dispersive powers of the two media are widely different.

All these deductions from the theory have been already verified by Sogani.

In the above discussion, we have not taken the effect of the changes produced in the wave-length. Actually γ is inversely proportional to λ^2 , so that it is larger for smaller wave-lengths and *vice versa*. This results in a reduction of the range of wave-lengths transmitted on the shorter wave-length side of λ_0 , and in an increase on the longer wave-length side.

From (13), the value of the attenuation factor is

$$\exp [-8\pi^3 N l (\mu - \mu_0)^2 a^4 / \lambda^2].$$

Now, if one assumes a close-packing of the droplets of the dispersed phase, then the total volume occupied by them is 74 per cent. of the total volume, so that

$$N = .74/(4\pi a^3/3) = 2.22/4\pi a^3.$$

If the packing is not so close, one can introduce a coefficient σ , called the "coefficient of packing", which is equal to the ratio of the actual volume occupied by the dispersed phase to the volume it would occupy in close packing. Then, $N = 2.22\sigma/4\pi a^3$, so that attenuation factor becomes

$$\exp [-4.44\pi^2\sigma l (\mu - \mu_0)^2 a/\lambda^2] = \exp [-22\sigma \cdot \frac{(\mu - \mu_0)^2}{\lambda^2} ld] \quad (16)$$

where d is the diameter of the droplet.

Sogani has performed some experiments to determine the attenuation coefficient, and found that

$$I_l = I_0 \exp [-B (\mu - \mu_0)^2 ld/\lambda^2]$$

which is of the same form as the one derived by us. However, for a close-packed emulsion, he found the value $B = 9$, which is much less than the theoretical value derived above. The discrepancy can partly be explained as due to the scattered light also entering the photometer, as suspected by Sogani himself, and also as due to the emulsion not being homogeneous but containing smaller droplets, both of which tend to decrease the attenuation coefficient. But it must also be noted that we have based our theory on the assumption of a random distribution of the particles, with no particular phase correlation. Such a state of affairs cannot be expected to occur in a close-packed emulsion, where one should expect the radiation from the next neighbours at least to be coherent.

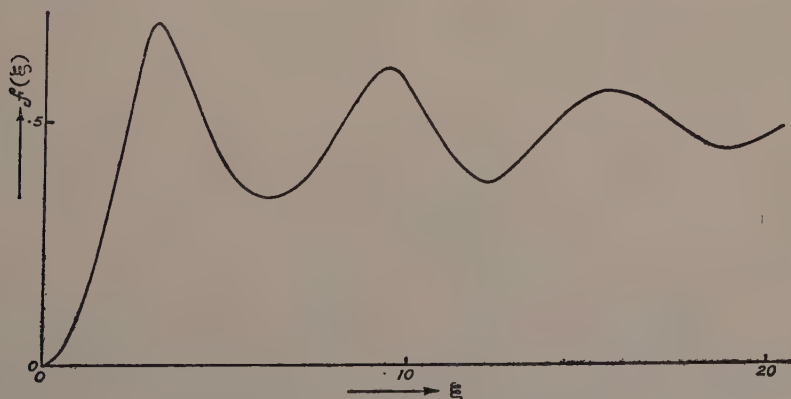


FIG. 1. Graph of $f(\xi)$ against ξ

As already remarked, the interesting phenomena exhibited by chromatic emulsions occur only for small values of ξ . An evaluation of γ for particle

sizes of about 0.003 cm., and a thickness 3 cm. of the emulsion shows that the range of values of ξ within which the light is transmitted is $|\xi| < 0.1$. Within this range, C_1' is evidently equal to $\xi^2/8$, the other terms being extremely small. However, it is interesting to examine what happens for much larger values of ξ . For these values, the full expression for C_1' can be evaluated from (6) which gives a curve of the type shown in Fig. 1. This curve is the same as Fig. 2 of (1943 *a*), and $f(\xi)$ is the same as the present C_1' . From the figure, it is easily seen that the range of phenomena shown by chromatic emulsions lies within the initial portion of the curve, where C_1' increases with ξ . But, when $\xi > 3$, $f(\xi)$ must actually diminish with increase of ξ , so that in this range, the attenuation coefficient must diminish, and the transmission must increase with increase of ξ . This phenomenon would appear worth looking for.

Incidentally, it may be noted that, in the study of transmission of light through water droplets, one is interested in the oscillating portion of the curve, while in the present case it is the limiting portion of the curve near $\xi = 0$ that is important.

3. Refractive Index of the Emulsion

In the last section, we have shown that the refractive index, n , of the emulsion is given by

$$n - \mu_0 = N\lambda a^2 S' \quad (9)$$

S' can also be expanded in powers of ξ as

$$S' = \xi/3 - \xi^3/30 + \dots \quad (17)$$

and for small values of ξ , which only occur in the region of transmission,

$$S' = \xi/3 = \frac{4\pi}{3} (\mu - \mu_0) \cdot \frac{a}{\lambda}.$$

Hence,
$$n - \mu_0 = \frac{4}{3} \pi a^3 \cdot N (\mu - \mu_0).$$

Now, $4\pi a^3 N/3$ is the total volume of the disperse phase, call it V_0 , contained in unit volume of the emulsion, so that

$$n - \mu_0 = V (\mu - \mu_0), \text{ or}$$

$$n = V\mu + (1 - V)\mu_0 = V\mu + V_0\mu_0, \quad (18)$$

where V_0 is the volume of the continuous phase. This shows that the refractive index of the emulsion is the same as that of an ordinary mixture of the two liquids. This is not surprising since, when the difference in the refractive indices of the two media is small, the actual nature of the boundary is unimportant, and the optical behaviour of the emulsion is, as if the two liquids were miscible.

Differentiating (18) with respect to λ one gets

$$dn/d\lambda = V d\mu/d\mu + V_0 d\mu_0/d\lambda \quad (19)$$

which gives the relation between the dispersion of the emulsion and those of the two components.

4. Intensity of the Diffracted Light

The amplitude of the diffracted light is given by expressions (1) to (4), where the integrals in the expression for X_1 have to be integrated. Denoting the integrals by C and S, our aim is to integrate them for finite values of η , so as to be applicable for the case when ξ is small. The method adopted in (1943 b) is not suitable in this case, and a new method is therefore used for the purpose.

Expand $\cos(\xi \cos \theta)$ and $\sin(\xi \cos \theta)$ in powers of $(\xi \cos \theta)$ as

$$\cos(\xi \cos \theta) = 1 - \frac{\xi^2}{(2)!} \cos^2 \theta + \frac{\xi^4}{(4)!} \cos^4 \theta - \dots + (-1)^p \frac{\xi^{2p}}{(2p)!} \cos^{2p} \theta + \dots$$

$$\sin(\xi \cos \theta) = \frac{\xi}{(1)!} \cos \theta - \frac{\xi^3}{(3)!} \cos^3 \theta + \dots + (-1)^p \frac{\xi^{2p+1}}{(2p+1)!} \cos^{2p+1} \theta + \dots$$

Then,

$$C = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p}}{(2p)!} \int_0^{\pi/2} J_0(\eta \sin \theta) \sin \theta \cos^{2p+1} \theta d\theta.$$

The integral in each one of the terms of the above series can be integrated, since it is of the standard form of Sonine's first integral, viz.,

$$\int_0^{\pi/2} J_\mu(z \sin \theta) \sin^{\mu+1} \theta \cos^{2\nu+1} \theta d\theta = \frac{2^\nu \Gamma(\nu+1)}{z^{\nu+1}} \cdot J_{\mu+\nu+1}(z)$$

with $\mu=0$ and $\nu=p$. Hence,

$$C = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p}}{(2p)!} \frac{2^p (p)!}{\eta^{p+1}} J_{p+1}(\eta). \quad (20)$$

Similarly, on expanding $\sin(\xi \cos \theta)$, S becomes

$$S = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p+1}}{(2p+1)!} \int_0^{\pi/2} J_0(\eta \sin \theta) \sin \theta \cos^{2p+2} \theta d\theta.$$

Here also, each one of the integrals is of the form of Sonine's integral with $\mu=0$ and $\nu=p+1/2$, so that

$$S = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p+1}}{(2p+1)!} \frac{2^{p+1/2} \Gamma(p+3/2)}{\eta^{p+3/2}} J_{p+3/2}(\eta) \quad (21)$$

On simplifying, and making the substitution $F_\mu(z) = J_\mu(z)/z^\mu$, we get

$$C = \sum_{p=0}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} F_{p+1}(\eta) \quad (22)$$

$$S = \sqrt{\frac{\pi}{2}} \xi \left[\sum_{p=0}^{\infty} (-1)^p \frac{1}{2^p (p)!} \xi^{2p} F_{p+3/2}(\eta) \right]. \quad (23)$$

The amplitude X is therefore

$$X = K \sin \chi [C - F_1(\eta)] - KS \cos \chi. \quad (24)$$

But, $C - F_1(\eta)$ is easily seen to be $= \sum_{p=1}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} F_{p+1}(\eta)$ which may be represented by $-C_1$. Then,

$$X = -KC_1 \sin \chi - KS \cos \chi. \quad (25)$$

We have thus developed X as a power series in ξ , which is convergent for all values of ξ and η (*vide* Appendix I). However, the expansion is useful only for small values of ξ , for which C_1 and S are rapidly convergent, so that the first one or two terms alone need be taken into account. Incidentally, it may be noted that on putting $\eta = 0$, C_1 and S become

$$C_1' = \xi^2/8 - \xi^4/144 + \dots$$

$$S' = \xi/3 - \xi^3/30 + \dots$$

which are identical with the values obtained by direct integration.

The intensity of the light diffracted by a single droplet is, from (25),

$$I = K^2 (C_1^2 + S^2).$$

Substituting for C_1 and S , and neglecting terms in ξ^4 and higher powers of ξ , this becomes*

$$I = \frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta). \quad (26)$$

The above expression relates to the intensity scattered by a single droplet in the direction ϕ . But the light reaching it, and the light diffracted by it have both to travel through the emulsion, and the total path will not differ from the thickness l of the emulsion, if ϕ is not large. Hence, the actual light coming out of the emulsion from one droplet is $I \exp(-\pi a^2 N l \xi^2/2)$. Also, if we take the droplets as distributed at random, then, the intensity of light diffracted out of unit volume of the emulsion in the direction ϕ is

$$I_\phi = N \frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta) \exp[-\pi a^2 N l \xi^2/2]. \quad (27)$$

* This expression can also be derived by introducing the approximations directly in equations (1) to (3) as shown in Appendix II.

This is the general expression for the intensity of the diffracted light. In the next two sections, we shall discuss its nature in detail.

5. Light Diffracted by Uniform Emulsions

In a uniform emulsion, the droplets of the dispersed phase will all be of the same size, so that a is a constant, and the only variable to be considered are the wavelength λ and the angle of scattering ϕ .

(a) Variation of intensity with angle of diffraction ϕ

If we use monochromatic light, then λ is a constant, so that ξ is fixed. Hence, I_ϕ is proportional to $F_{3/2}^2(\eta)$. This quantity is plotted in Fig. 2, from which it will be seen that the intensity is zero for $\eta = 4.5, 7.75, \dots$ and is a maximum for $\eta = 0, 6.0, 9.1, \dots$. Since $\eta = 2\pi(a/\lambda) \sin \phi$, alternate bright and dark rings must be visible in the diffraction pattern

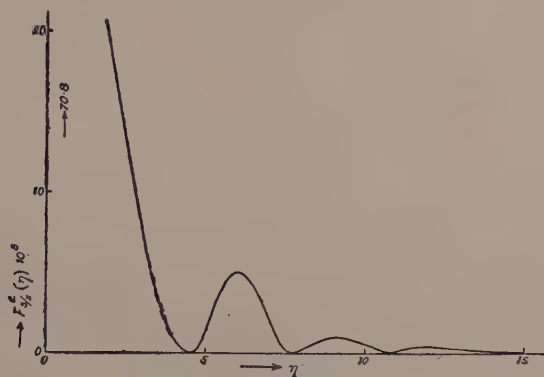


Fig. 2. Graph of $F_{3/2}^2(\eta)$ against η .

corresponding to the above values of η . The relative intensities of the first three bright rings are given by $I_1 : I_2 : I_3 = 5 : 1 : 0.25$. For $a = 2 \times 10^{-3}$ and $\lambda = 6 \times 10^{-5}$, the angle of diffraction for the first bright ring comes out to be $\phi = 0.028^\circ$. In fact, Sogani, using a homogenized emulsion, found a value 0.025° for the angular radius of the first ring. The agreement of this with the theoretical value is not to be stressed, for the type of pattern observed by Sogani had a minimum of intensity at the centre, while our theory requires a maximum. The effect observed by Sogani is similar to the diffraction of X-rays by liquids; on account of the fact that the droplets in a homogenized emulsion have a quasi-regularity in arrangement, interference effects arise in addition to the diffraction by individual droplets.

(b) Variation of the Intensity with Wavelength

From the expression (27), it is seen that the intensity $I_\phi \propto \xi^2 e^{-\beta^2 \xi^2} F_{3/2}^2(\eta)$ where $\beta = \pi a^2 N / 2$. Since $F_{3/2}^2(\eta)$ gives only a variation with angle, the

intensity of the ring system as a whole can be said to be proportional to $\xi^2 e^{-\beta \xi^2}$. This quantity is equal to zero at $\xi = 0$, increases with ξ up to $\xi^2 = 1/\beta$ and then decreases again. Hence, no ring system must be visible at $\lambda = \lambda_0$, for which $\xi = 0$. On either side, the rings must appear, and at first increase in intensity as the wavelength is removed more and more from λ_0 , until it reaches a maximum. Thereafter, the intensity must diminish again until, when λ is far removed from λ_0 , no rings must be visible. All these have been experimentally verified by Sogani.

If now, white light is used, and the spectrum of the light diffracted at an angle is observed, then the intensity will vary as $\xi^2 e^{-\beta \xi^2}$, being zero for $\lambda = \lambda_0$, and being a maximum for the values of λ for which

$$\xi^2 = 1/\beta \text{ or } (\mu - \mu_0)^2 = 1/\gamma. \quad (28)$$

The function $\xi^2 e^{-\beta \xi^2}$ has been plotted in Fig. 3 against ξ as ordinate, for the value 2 of β . This shows the nature of the intensity distribution in the spectrum of the diffracted light.

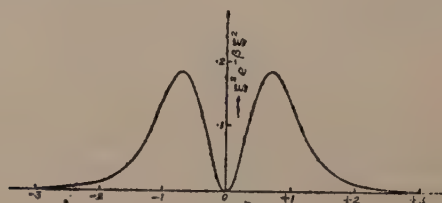


Fig. 3. Graph of $\xi^2 e^{-\beta \xi^2}$ against ξ .

(c) Variation of the Size of the Rings with the Wavelength

Since $\eta = 2\pi a \sin(\phi)/\lambda$, it is evident that as λ increases, the size of the rings must increase. Thus, the width of the ring system must *continuously* increase with the wavelength, although its intensity is a minimum at λ_0 , and increases on either side. This fact has also been noted by Sogani.

Another interesting fact, also noted by Sogani, is that "the size of the rings... is, strangely enough, uninfluenced by the thickness of the emulsion". This, however, is a natural conclusion from our theory, for N and l occur only in the exponential in (27), and do not occur in the function $F_{3/2}^2(\eta)$, so that, for the same reason as explained in Section (4) of (1943 b), the size of the rings must be uninfluenced by the thickness (l) or the concentration (N) of the emulsion.

6. Phenomena with Non-Uniform Emulsions

In a non-uniform emulsion, all the droplets are not of the same size, so that the phenomena are a little complicated. In the preceding section,

it has been shown that the intensity diffracted in a direction ϕ is $\frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta)$.

Hence, the intensity is directly proportional to the sixth power of the radius of the droplet. But the width of the bright central portion is determined by the value of η , which must be less than 4.5, *i.e.*, the range of angles covered by the central bright portion is given by $\sin \phi < 4.5 \lambda / 2\pi a$. Thus, the width of this portion diminishes with increase of the size of the particle. Hence, it is clear that, for any angle of diffraction ϕ_1 , the maximum intensity will be due to particles of a certain radius a_1 (say), those having a larger or a smaller radius, giving only a less intensity. This can be proved as follows:

If the angle of diffraction is ϕ_1 , then $\eta = 2\pi \sin(\phi_1) a / \lambda$, and $\xi = 4\pi(\mu - \mu_0) a / \lambda$, so that for a particular wavelength, ξ is a constant multiple of η . Also, K is a constant multiple of ξ , so that

$$I_\phi \propto \eta^6 J_{3/2}^2(\eta) / \eta^3 \propto \eta^3 J_{3/2}^2(\eta) \quad (29)$$

Hence I_ϕ is a maximum for that value, η_0 , of η for which $\eta^3 J_{3/2}^2(\eta)$ is a maximum. The radius of the droplet corresponding to this is given by $2\pi \sin(\phi_1) a_1 / \lambda = \eta_0$, or

$$a_1 = \lambda \eta_0 / 2\pi \sin \phi_1. \quad (30)$$

Thus, for every angle ϕ_1 , the predominant portion of the diffracted light is due to particles of radius a_1 given by (30), which is smaller for larger angles.

In Section 5, we have shown that the spectrum of the diffraction light always consists of a minimum at $\lambda = \lambda_0$, and two maxima on either side corresponding to

$$(\mu - \mu_0)_{\max}^2 = 1/\gamma. \quad (28)$$

But γ is a function of a_1 , so that it varies with the angle of diffraction in the present case. Since $\gamma = 8\pi^3 N I \cdot a^4 / \lambda^2$, for an angle of diffraction ϕ_1 ,

$$\gamma = \frac{8\pi^3 N I \lambda^4 \eta_0^4}{16 \pi^4 \sin^4 \phi_1 \lambda^2} = \frac{N I \eta_0^4 \lambda^2}{2\pi \sin^4 \phi_1}. \quad (31)$$

Thus, other quantities being the same,

$$(\mu - \mu_0)_{\max} \propto \sin^2 \phi_1. \quad (32)$$

If, in the immediate neighbourhood of λ_0 , we assume a direct proportionality between $(\mu - \mu_0)$ and $(\lambda - \lambda_0)$, then it at once follows that the spectral range between the two maxima, *viz.*,

$$2(\lambda - \lambda_0)_{\max} \propto 2(\mu - \mu_0)_{\max} \propto \sin^2 \phi_1, \quad (33)$$

Thus, as the angle of diffraction ϕ is increased, the central dark portion in the spectrum of the diffracted light must widen, and correspondingly the bright portions also must broaden. This result from the theory is remarkably confirmed by Sethi's observations, where a progressive broadening of

the spectrum was found as the direction of observation was taken further away from the incident direction.

In the discussion given above, we have neglected the effect of the variation of λ . On introducing this also, $\gamma \propto \lambda^2/\sin^4 \phi_1$, so that

$$(\mu - \mu_0)_{max.} \propto \sin^2 \phi_1/\lambda. \quad (34)$$

Thus, the quantity $(\mu - \mu_0)_{max.}$ varies continuously with λ , being greater for smaller wavelengths. Hence, at large angles, where an appreciable portion of the spectrum is transmitted, there must be a further broadening on the shorter wavelength side, and an opposite effect on the longer wavelength side. So also, the actual intensity is proportional to λ^{-4} , which enormously increases the intensity for smaller wavelengths. For both these reasons, the spectrum must show an asymmetry, greater intensity being concentrated on the shorter wavelength side of the transmission band.

Another assumption made in the above discussion is that droplets of all sizes are present in the emulsion. Actually, there must be an upper and a lower limit to the size of the droplets. This fact limits the minimum and the maximum widths of the spectrum. Between these limits, however, the width must regularly increase with the angle of diffraction.

My sincere thanks are due to Prof. Sir C. V. Raman, for suggesting the problem and for the keen interest that he took in it.

Summary

A theory of the optical phenomena exhibited by chromatic emulsions as also those observed in the Christiansen experiment has been worked out, *de novo*, on the basis of the diffraction of light by a sphere immersed in a medium of nearly the same refractive index. Expressions are derived both for the intensity of the transmitted light, and of the light diffracted in other directions. These are discussed in relation to the intensity and the spectral nature of the light and it is shown that the theory can satisfactorily account for the various phenomena observed by Sethi and Sogani.

REFERENCES

1. Christiansen .. *Ann. d. Phys.*, 1884, **23**, 298.
2. Holmes, H. N., and
Cameron, D. H. .. *Journ. Am. Chem. Soc.*, 1922, **44**, 71.
3. Ramachandran, G. N. *Proc. Ind. Acad. Sci. A*, 1943 *a*, **17**, 171.
4. ————— .. *Ibid.*, 1943 *b*, **17**, 202.
5. Rayleigh, Lord .. *Phil. Mag.*, 1885, **20**, 358.
6. ————— .. *Sci. Papers*, 1899, **IV**, 392.
7. Sethi, N. K. .. *Proc. Ind. Assoc. Cult. Sci.*, 1921, **6**, 124.
8. Sogani, C. M. .. *Phil. Mag.*, 1926, **1**, 321.

APPENDIX I

Note on the Convergency of the Series C_1 and S

$$\text{Let } C_1 = \sum u_p = \sum_{p=1}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} \frac{J_{p+1}(\eta)}{\eta^{p+1}}.$$

$$\text{Then } \left| \frac{u_{p+1}}{u_p} \right| = \frac{2(p+1)}{(2p+1)(2p+2)} \cdot \frac{\xi^2}{\eta} \cdot \frac{J_{p+2}(\eta)}{J_{p+1}(\eta)}.$$

But, for large values of p , $J_{p+2}(\eta)/J_{p+1}(\eta) = \eta/2(p+2)$, so that

$$\text{Lt}_{p \rightarrow \infty} \left| \frac{u_{p+1}}{u_p} \right| = \text{Lt}_{p \rightarrow \infty} \frac{\xi^2}{(2p+1)(2p+2)} \cdot \frac{(p+1)}{(p+2)} \text{ which is } = 0, \text{ if } \xi \text{ is finite.}$$

Hence $\sum u_p$ is absolutely convergent.

In the same way, putting

$$S = \sum v_p = \sum_{p=0}^{\infty} (-1)^p \frac{1}{2^p (p)!} \xi^{2p+1} \frac{J_{p+3/2}(\eta)}{\eta^{p+3/2}},$$

$$\left| \frac{v_{p+1}}{v_p} \right| = \frac{1}{2p} \cdot \frac{\xi^2}{\eta} \cdot \frac{J_{p+5/2}(\eta)}{J_{p+3/2}(\eta)}.$$

Substituting the value for $J_{p+5/2}(\eta)/J_{p+3/2}(\eta)$ for large values of p , namely $\eta/(2p+5)$,

$$\text{Lt}_{p \rightarrow \infty} \left| \frac{v_{p+1}}{v_p} \right| = \text{Lt}_{p \rightarrow \infty} \frac{\xi^2}{2p(2p+5)}, \text{ which is also } = 0, \text{ if } \xi \text{ is finite.}$$

Thus, $\sum v_p$ is also absolutely convergent.

Hence, both C_1 and S are convergent for all values of ξ and η .

APPENDIX II

A Simple Derivation of the Expression for the Intensity

As already remarked, one is interested only in small values of ξ in the study of chromatic emulsions, in which case $\cos(\xi \cos \theta) \simeq 1$ and $\sin(\xi \cos \theta) \simeq (\xi \cos \theta)$. Substituting these in (1) to (3),

$$\begin{aligned} X = & K \sin \chi \left[\int_0^{\pi/2} J_1(\eta \sin \theta) \sin \theta \cos \theta d\theta - J_1(\eta)/\eta \right] \\ & - K \cos \chi \int_0^{\pi/2} J_0(\eta \sin \theta) (\xi \cos \theta) \sin \theta \cos \theta d\theta \end{aligned}$$

The quantity within the square brackets vanishes, and using Sonine's integral with $\mu=0$ and $\nu=1/2$, the second term becomes

$$- \sqrt{\frac{\pi}{2}} K \xi J_{3/2}(\eta)/\eta^{3/2},$$

Hence, the intensity is

$$I = \frac{\pi}{2} K^2 \xi^2 J_{3/2}^2(\eta)/\eta^3,$$

which is identical with expression (26).

A TAUBERIAN THEOREM AND ITS APPLICATION TO CONVERGENCE OF FOURIER SERIES

BY K. S. K. IYENGAR

Received August 4, 1942

Received in revised form April 6, 1943

1. LET $\left(1 + \frac{x}{2} + \frac{x^2}{3} + \dots + \frac{x^n}{n+1} + \text{to } \infty\right)^k = \sum_0^\infty b_{k,n} x^n$, k being a positive integer and let $\sum_{r=0}^n b_{k,r} = B_{k,n}$. Whenever $\sum_0^n b_{k,n-r} \cdot S_r / B_{k,n}$ converges to a limit say S as $n \rightarrow \infty$, I shall indicate that fact by the symbol $S_n \rightarrow S (N, k)$ as $n \rightarrow \infty$. (1.1)

The main object of this note is the proof of two theorems (I and II) the first of these being a Tauberian theorem on mean convergence or summability (N, k) , the second being the summability $(N, 1)$ of the Fourier series of a summable (L) function $f(x)$ at a point x_0 at which, $\{(f(x_0 + h) - f(x_0)) \cdot \log |h|\} \rightarrow 0$ as $h \rightarrow 0$. From these two theorems, which are new, it is noteworthy that the truth of the convergence criterion, of Hardy and Littlewood (1932) of the Fourier series of a summable function $f(x)$ at a point x_0 , namely (1) $\{(f(x_0 + h) - f(x_0)) \log |h|\} \rightarrow 0$ as $h \rightarrow 0$ (2) the Fourier coefficients of $f(x)$ or order $n \leq A \cdot n^\delta$, ($A > 0$, $\delta > 0$), (1.2) follows at once. Before proceeding further it should be noted that summability (N, k) is more stringent than Cesaro means of any positive order, for it can be established that (N, k) implies (C, r) when $k > 0$ and $r > 0$, but not conversely.

2. Statement of Theorems

THEOREM I. If $S_n \rightarrow S (N, k)$ k being a positive integer and $S_n - S_{n-1} = \delta S_n \leq A n^{-\mu}$ ($A > 0$, $1 > \mu > 0$), then S_n converges ordinarily to S . (2.1)

Note 1.—If $\mu = 1$, in view of the remark at the end of 1, the theorem reduces itself to Cesaro-Tauber theorem.

Note 2.—As we should expect from Hardy-Littlewood's paper,¹ we should be able to prove that whenever $S_n \rightarrow S (N, k)$, k being a positive integer then $S_n \rightarrow S$ also by Valeron means (V, k_1) of order k_1 where

$$1 \leq k_1 < 2, \text{ i.e., } \frac{1}{\sqrt{\pi \cdot M}} \sum_{p=0}^{\infty} S_p e^{\frac{-(p-n)^2}{M}} \rightarrow S \text{ as } n \rightarrow \infty, M = 2 \cdot n^{2-k_1}; \quad (2.2)$$

then the Tauberian Theorem I follows. But the direct proof of Theorem I, which is given here, apart from its intrinsic interest is much simpler than the proof of the fact that (N, k) implies (V, k_1) for k a positive integer and $1 \leq k_1 < 2$. However for completeness the fact of (N, k) implying (V, k_1) is stated as Theorem III, and the proof of this theorem under the title "On the relation between summability by Norlund means of a certain type and summability by Valeron Means," will appear shortly in the *Journal of the Mysore University*.

THEOREM II. If $f(x)$ be a periodic (2π) L integeble function and $\{(f(x_0 + h) - f(x_0)) \log |h|\} \rightarrow 0$ as $h \rightarrow 0$, then the Fourier series of $f(x)$ at x_0 is summable $(N, 1)$ to $f(x_0)$. (2.3)

THEOREM III. If $S_n \rightarrow S$, (N, k) k being a positive integer then

$$S_n \rightarrow S, (V, k_1) \quad 1 \leq k_1 < 2 \text{ (for all such } k_1). \quad (2.4)$$

3. Proof of Preliminary Lemmas

Lemma I. Let $b_{k,n}$ and $B_{k,n}$ be as in (1.1), and $a_{k,n}$ be defined by

$$\left(1 - \sum_{r=1}^{\infty} a_{k,r} x^r\right) \left(\sum_{r=0}^{\infty} b_{k,r} x^r\right) = 1 \quad (3.1)$$

$$\text{then } \left. \begin{aligned} (a) \quad b_{k,n} &= \sum_{r=1}^n a_{k,r} \cdot b_{k,n-r}, & (b) \quad B_{k,n} &= 1 + \sum_{r=1}^n a_{k,r} B_{k,n-r} \\ (c) \quad b_{k,n} &= O\left(\frac{(\log n)^{k-1}}{n}\right) & (d) \quad a_{k,n} &= O\left(\frac{1}{n \cdot (\log n)^{1+k}}\right). \end{aligned} \right\} \quad (3.2)$$

(a) and (b) follow from the definition in (3.1) and (c) can be deduced by induction from

$$b_{k,n} x^n = \left(1 + \sum_{r=1}^{\infty} \frac{x^r}{r+1}\right)^k. \quad (3.3)$$

Proof of (d) of (3.2)

Let $V_n(a) = \frac{(1-a)(2-a) \cdots (n-1-a)}{[n]}$; we shall here establish by induction that

$$a_{k,n} = \frac{1}{[k-1]} \int_0^1 V_{n-k} \cdot a^k \cdot da + O\left(\frac{1}{n^2 \cdot (\log n)^2}\right). \quad (3.4)$$

$[k \geq 1]$

Let $I = \int_0^1 (1-x)^a \cdot \frac{(1-a)^{k-1}}{[k-1]} da$; integrating directly and expanding

$(1-x)^a$ and integrating term by term, we obtain

$$I = \frac{(1-x) - \sum_{r=0}^{k-1} \frac{(\log 1-x)^r}{|r|}}{(\log 1-x)^k} \\ = \frac{1}{|k|} - \sum_{n=1}^{\infty} \left[\int_0^1 V_n(a) \cdot a \cdot \frac{(1-a)^{k-1}}{|k|-1} da \right] \cdot x^n \quad (3.5)$$

Multiplying by $(-x)^{k-1}$, we obtain from 3.5

$$\left(\frac{-x}{\log 1-x} \right)^k = \sum_{r=1}^{k-1} \frac{(-x)^{k-1-r}}{|k-r|} \cdot \left(\frac{-x}{\log 1-x} \right)^r \\ + (-1)^{k-1} \left\{ \frac{x^{k-1}}{|k|} - \sum_{n=1}^{\infty} \left\{ V_n(a) \cdot a \cdot \frac{(1-a)^{k-1}}{|k|-1} \cdot da \right\} x^{n+k-1} \right\} \quad (3.6)$$

From 3.1 and 1.1 definitions we have

$$\left(\frac{-x}{\log 1-x} \right)^k = 1 - \sum_{n=1}^{\infty} a_{k,n} x^n \quad (3.7)$$

so that for $n > k$ we obtain from 3.6

$$a_{k,n} = a_{k-1,n} - \frac{a_{k-2,n-1}}{|2|} + \dots + \dots \\ + (-1)^{k-2} a_{1,n-k+2}^{\frac{1}{|k-1|}} + (-1)^{k-1} \cdot \int_0^1 V_{n-k+1}^{(a)} \cdot a \cdot \frac{(1-a)^{k-1}}{|k|-1} da. \quad (3.8)$$

It is easy to see that (3.4) is true for $k=1$; assume it true for $k=1, 2, \dots, k-1$, then from 3.8

$$a_{k,n} = \int_0^1 V_{n-k+1} \left(\frac{a^{k-1}}{|k-2|} - \frac{a^{k-2}}{|2| |k-3|} + \dots + \frac{(-1)^{k-2} \cdot a}{|k-1|} \right. \\ \left. + (-1)^{k-1} \cdot a \cdot \frac{(1-a)^{k-1}}{|k|-1} \right) da + O \left(\frac{1}{n^2 (\log n)^2} \right) \quad (3.9)$$

$$= \int_0^1 V_{n-k+1}^{(a)} \cdot a^k da + O \left(\frac{1}{n^2 (\log n)^2} \right). \quad (3.10)$$

Now $V_n \leq \frac{K}{n^{1+\alpha}}$ and $V_{n-k+1} = V_{n-k} \left\{ 1 + O \left(\frac{1}{n} \right) \right\}$.

Hence

$$\int_0^1 V_{n-k+1} a^k da = \int_0^1 V_{n-k} a^k da + O \left\{ \frac{1}{n} \cdot \int_0^1 V_n a^k da \right\} \\ = \int_0^1 V_{n-k} a^k da + O \left(\frac{1}{n^2 (\log n)^{1+k}} \right) \quad (3.11)$$

$$\text{Hence } a_{k,n} = \int_0^1 V_{n-k} a^k \cdot da + O\left(\frac{1}{n^2 \cdot (\log n)^2}\right) \text{ for } k \geq 1 \quad (3.12)$$

thus proving (3.4)

From (3.12)

$$\begin{aligned} a_{k,n} &= O\left(\frac{1}{n \cdot (\log n)^{1+k}}\right) + O\left(\frac{1}{n^2 \cdot (\log n)^2}\right) \\ &= O\left(\frac{1}{n \cdot (\log n)^{1+k}}\right) \text{ thus proving (d) of (3.2)} \end{aligned} \quad (3.13)$$

4. Lemma II

If $S_n \rightarrow 0$ (N, k) where k is a positive integer and $N = N_n = [K \cdot n^\delta]$ where $0 > \delta > 1$, and K is a positive fixed number, then

$$\left[\sum_{r=0}^n b_{k,r+N} \cdot S_{n-r} / \sum_{r=0}^n b_{k,r+N} \right] \rightarrow 0 \text{ as } n \rightarrow \infty \quad (4.1)$$

[Since in what follows k is a fixed integer, a_n , b_n , and B_n , shall stand for $a_{k,n}$, $b_{k,n}$ and $B_{k,n}$ respectively and whenever x_n and y_n are of the same order we shall indicate by $x_n = O(S_n)$ (big O) and whenever $\frac{x_n}{y_n} \rightarrow 0$, we indicate by $x_n = o(y_n)$ (little O).]

From 3.2 and the condition about N it is easy to deduce that

$$\sum_{r=0}^n b_{k,r+N} = \sum_{r=0}^n b_{r+N} \text{ (by, 4.2)} = O(B_{k,n}) = O[(\log n)^k] \quad (4.3)$$

$$\text{and we have therefore to prove } \sum_{r=0}^n b_{r+N} S_{n-r} = o(B_n). \quad (4.4)$$

Let $\sum_{r=0}^n b_r S_{n-r} / B_n = y_n$; then from relation (3.1) we obtain

$$S_n = B_n y_n - \sum_{r=1}^n a_r \cdot B_{n-r} y_{n-r}. \quad (4.5)$$

Substituting (4.5) in the l.h.s. of 4.4 we obtain

$$\sum_{r=0}^n b_{r+N} S_{n-r} = \sum_{r=0}^n A_{n,r} \cdot B_r \cdot y_r \quad (4.6)$$

$$\text{where } A_{n,r} = b_{n-r+N} - a_1 b_{n-r-1+N} - a_{n-r} b_N. \quad (4.7)$$

We shall now consider r.h.s of 4.6 in three parts.

$$\sum_{r=0}^n A_{n,r} \cdot B_r \cdot y_r = \sum_{r=0}^{r=n_1} + \sum_{r=n_1+1}^{[n-N^{1-\epsilon}]} + \sum_{r=[n-N^{1-\epsilon}]+1}^n = A + B + C. \quad (4.8)$$

where n_1 is a conveniently chosen fixed integer.

Since by (3.2) $\sum |a_r|$ converges, we have from (4.7) and (3.2)

$$|A_{n,r}| \leq O\left(\frac{(\log N)^{k-1}}{N}\right). \quad (4.9)$$

$$\text{Hence } |C| \leq K \cdot \sum_{0 \leq n-r \leq N^{1-\epsilon}} A_{n,r} B_r \leq K' \cdot N^{1-\epsilon} \cdot \frac{(\log N)^{k-1}}{N} \cdot B_n = O(B_n). \quad (4.10)$$

Consider now B. From 4.7 and 3.2 (a) we have

$$A_{n,r} = a_{n-r+1} b_{N-1} + \dots + a_{n-r+N} \quad (4.11)$$

Since in B

$$n-r \geq N^{1-\epsilon} - 1 \text{ and } a_n = O\left(\frac{1}{n \cdot (\log n)^{1+k}}\right) \text{ and } b_n = O\left(\frac{(\log n)^{k-1}}{n}\right)$$

and $N = [K \cdot n^\delta]$ from, (3.2)
 $0 < \delta < 1$

we obtain from (4.11) $|A_{n,r}| \leq K_1 \sum_{p=1}^{p=N} \frac{(\log N - p + 2)^{k-1}}{(N - p + 2)(q + p)[\log(q + p)]^{1+k}}$
where $q = n - r$.

$$\leq \frac{K_2}{(\log n)^2} \cdot \sum_{p=1}^{p=N} \frac{1}{(q + p)(N - p + 2)} \quad (4.12)$$

$$\leq \frac{K_3}{\log n \cdot (N + q + 2)} \quad (4.13)$$

$$\begin{aligned} \text{so that } |B| &\leq \text{Max of } y_r \cdot \frac{K_3 \cdot B_n}{\log n} \cdot \sum_{n_1+1 \leq r \leq n-N^{1-\epsilon}}^{q=n} \frac{1}{N+2+q} \\ &\leq \text{Max of } y_r \cdot K_4 \cdot B_n. \end{aligned} \quad (4.14)$$

$n_1+1 \leq r$

Consider now A. From (4.13) for fixed r as $n \rightarrow \infty$ we have

$$|A_{n,r}| \leq \frac{K_4}{n \cdot \log n} \quad (4.15)$$

$$\text{so that for fixed } r \quad A_{n,r} \cdot B_r = O(B_n) \quad (4.16)$$

so that from (4.10), (4.14) and (4.16) and hypothesis that $y_n \rightarrow 0$ as $n \rightarrow \infty$ (i.e., 4.1) we obtain $A + B + C = O(B_n)$, thus proving 4.4 and establishing Lemma II. (4.17)

5. Proof of Theorem I

Without loss of generality we assume that

$$\sum_0^n b_{n-r} S_r / B_n \rightarrow 0, \text{ as } n \rightarrow \infty. \quad (5.1)$$

[As in 4, a_n, b_n, B_n stand for $a_{k,n}, b_{k,n}$ and $B_{k,n}$].

$$\text{Suppose } \liminf S_n = -b, \quad b > 0 \quad (5.2)$$

Then there exists a sequence $n_0 < n_1 < \dots < n_r \rightarrow \infty$ such that $S_{n_r} \leq -b_1$
 $0 < b_1 < b$. (5.3)

Since $\delta S_n \leq A \cdot n^{-\mu}$ ($0 < \mu < 1$) it can be easily shown that

$$S_n \leq -b_1/2 \text{ when } n_r \leq n \leq n_r + N_{n_r} \quad (5.4)$$

$$\text{where } N_{n_r} = N = \left[\frac{b_1}{2} \cdot \frac{n^{\mu}}{A} \right]$$

$$\text{Now } \sum_{r=0}^{n+N} b_{n+N-r} S_r = \sum_{r=0}^{n+N} S_r + \sum_{r=n+1}^{n+N} S_r = \Sigma_1 + \Sigma_2 \quad (5.5)$$

$$\text{From Lemma II } \Sigma_1 = 0 \text{ (} B_{n+N} \text{)}. \quad (5.6)$$

By taking $n = n_r$, in view of 5.4

$$\text{we have } \Sigma_2 \leq -\frac{b_1}{2} \cdot \sum_{r=n+1}^{n+N} b_{n+N-r} = -\frac{b_1}{2} \cdot \sum_{p=0}^{N-1} b_p = -\frac{b_1}{2} \cdot B_{N-1}. \quad (5.7)$$

In view of condition about N , it can be shown that $B_{N-1} \geq K_1 \cdot B_{n+N}$ (5.8)
 where K_1 is a positive constant.

Hence $\Sigma_2/B_{n+N_{n_r}} \leq -\frac{b_1}{2} \cdot K_1$ so that

$$\liminf \frac{\sum_{r=0}^n b_{n-r} S_r}{B_n} \leq -\frac{b_1}{2} K_1 \text{ contradicting 5.1.} \quad (5.9)$$

Hence $\liminf S_n = 0$, the case of $\liminf S_n = -\infty$ being easily disposed of. (5.10)

similarly $\limsup S_n = 0$, thus establishing Theorem I. (5.11)

6. Proof of Theorem II

Let $S_n = \sum_0^n (a_r \cos rx + b_r \sin rx)$, a_r, b_r , being the Fourier coefficients of $f(x)$, and $\psi(t) = \frac{f(x_0+t) + f(x_0-t) - 2f(x_0)}{2}$. (6.1)

$$\text{Then } S_n(x_0) - f(x_0) = \frac{1}{\pi} \int_0^\pi \psi(t) \cdot \frac{\sin(n+\frac{1}{2})t}{\sin t/2} \cdot dt = \frac{1}{\pi} \int_0^\delta + \epsilon(n, \delta)$$

where δ is so chosen that $|\psi(t) \log t| \leq \epsilon$ $0 \leq t \leq \delta$; $\epsilon(n, \delta) \rightarrow 0$ as $n \rightarrow \infty$ (6.2)

$$\text{Now } \sum_{r=0}^n \frac{S_{n-r}(x_0)}{r+1} \Big/ \sum_{r=0}^n \frac{1}{r+1} - f(x_0) = \frac{1}{\pi L_n} \int_0^\delta \psi(t) \cdot \frac{K_n(t)}{\sin t/2} dt + \epsilon'(n, \delta) \quad (6.3)$$

$$\text{where } K_n(t) = \sum_{r=0}^n \frac{\sin(r+\frac{1}{2})t}{n+1-r}, \text{ and } L_n = \sum_{r=0}^n \frac{1}{1+r} \quad (6.4)$$

We shall first prove that

$$\left. \begin{aligned} \left| \frac{K_n(t)}{\sin t/2} \right| &\leq L_n \cdot 2n + 1 \text{ in } 0 \leq t \leq \frac{\pi}{n} \\ \text{and } |K_n(t)| &\leq K |\log t| \text{ in } \frac{\pi}{n} \leq t \leq \delta < 1 \end{aligned} \right\} \quad (6.5)$$

The first part follows from the fact that $\left| \frac{\sin pt}{\sin t} \right| \leq p$ when p is an integer.

To prove the second part we note that

$$\begin{aligned} K_n(t) &= \text{Imaginary part of } \left\{ -e^{-i(n+3/2)t} \cdot \sum_{p=1}^{n+1} \frac{e^{ipt}}{p} \right\} = \\ &= \text{Imaginary part of } \left\{ +e^{-i(n+3/2)t} \cdot \left(\log(1 - e^{it}) + \sum_{p=n+2}^{\infty} \frac{e^{ipt}}{p} \right) \right\} \\ &= \text{Imaginary part of } \left\{ e^{-i(n+3/2)t} (P_1 + P_2) \right\} \end{aligned} \quad (6.6)$$

Now $|P_1| = O\{|\log t|\}$ when $0 \leq t \leq \delta < 1$

and in $\frac{\pi}{n} \leq t \leq \delta < 1$ $|P_2| \leq \frac{K}{n \cdot t} = O(1)$, so that second part of 6.5 is established. (6.7)

$$\text{Now } \int_0^{\delta} \psi(t) \frac{K_n(t)}{\sin t/2} dt = \int_0^{\pi/n} + \int_{\pi/n}^{\delta}$$

(6.2) and (6.5) imply that $\left| \int_0^{\pi/n} \right| \leq K \cdot \epsilon \cdot L_n$ and

$$\left| \int_{\pi/n}^{\delta} \right| \leq K_1 \int_{\pi/n}^{\delta} \frac{|\psi(t) \log t|}{t} dt \leq K_2 \cdot \epsilon \cdot \log n \quad (6.8)$$

(6.3) and (6.8) implies that $S_n(x_0) \rightarrow f(x_0)$, $(N, 1)$ thus establishing Theorem II.

REFERENCES

1. Hardy and Littlewood .. "New Convergence Criteria for Fourier Series," *Journal of the London Mathematical Society*, October 1932, 252-56.
2. C. Valeron .. "Remarques sur la summation des series divergentes par la methodes des, M. Borel," *Rend di. Palermo*, 1917, 42, 267-84.

ON ARITHMETIC FUNCTIONS

BY P. KESAVA MENON

(*Annamalai University*)

Received September 29, 1942

(Communicated by Prof. A. Narasinga Rao, F.A.Sc.)

Introduction

IN a paper on the theory of multiplicative arithmetic functions R. Vaidyanathaswamy has investigated two operations on arithmetic functions—‘Composition’ and ‘Compounding’. In the same paper he has introduced the notion of a ‘principal function’ and has applied it to prove an interesting theorem on multiplicative functions which are functions of the g.c.d. of the arguments, the proof being by the method of ‘generating series’. The objects of the present paper are (1) to study an operation which generalizes composition and compounding, (2) to study in detail principal functions, to give a purely arithmetic proof of Vaidyanathaswamy’s result mentioned above and to obtain other similar results, (3) to evaluate certain multiple Dirichlet series, and (4) to evaluate certain multiple Lambert series.

The notions and notations in Vaidyanathaswamy’s paper are employed here.

Section 1. A Generalised Composition.

1. Let (D) denote the matrix

$$\begin{pmatrix} d_{11} & \dots & d_{1r} \\ \vdots & & \vdots \\ d_{s1} & \dots & d_{sr} \end{pmatrix}$$

and let f and ψ be two arithmetic functions of a $(r \times s)$ matrix set of arguments. Consider the function

$$\Sigma f(D),$$

the summation being for all divisions d_{ij} such that $\prod_{i=1}^s d_{ij} = M_j$ ($j = 1, 2, \dots, r$) and $\psi(D) = 1$. We shall show that this operation on f includes composition and compounding as particular cases.

Let the number of rows in the matrix be two and suppose that

$$f \begin{pmatrix} M_1, \dots, M_r \\ N_1, \dots, N_r \end{pmatrix} = f_1(M_1, \dots, M_r) \times f_2(N_1, \dots, N_r).$$

If we take ψ to be E (the function whose value is unity for all values of the arguments) it is clear that the above operation reduces to the composition of f_1 and f_2 ($f_1 \cdot f_2$).

Let $g(M, N)$ denote the greatest common divisor (g.c.d.) of M and N . If we take $\psi \left(\begin{smallmatrix} M_1, & \dots, & M_r \\ N_1, & \dots, & N_r \end{smallmatrix} \right)$ to be $\prod_{i=1}^r g(M_i, N_i)$, then it can easily be seen that the generalized operation is simply the compounding of f_1 and f_2 ($f_1 \oplus f_2$).

THEOREM 1: If f and ψ are multiplicative functions the latter being positive integral valued, then

$$\sum_{\psi(D)=1} f(D) = F(M_1, \dots, M_r)$$

$$\prod_{i=1}^s d_{ig} = M_g \quad (g=1, \dots, r)$$

is a multiplicative function of r arguments.

Proof.—Let $\prod_{i=1}^r M_i$ be prime to $\prod_{i=1}^r N_i$ and let (G) , (DG) denote the matrices

$$\begin{pmatrix} \delta_{11}, & \dots, & \delta_{1r} \\ \vdots & & \vdots \\ \delta_{s1}, & \dots, & \delta_{sr} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} d_{11} \delta_{11}, & \dots, & d_{1r} \delta_{1r} \\ \vdots & & \vdots \\ d_{s1} \delta_{s1}, & \dots, & d_{sr} \delta_{sr} \end{pmatrix}$$

respectively. Then it follows that

$$F(M_1 N_1, \dots, M_r N_r) = \sum_{\psi(DG)=1} f(DG)$$

$$\prod_{i=1}^s d_{ig} = M_g, \quad \prod_{i=1}^s \delta_{ig} = N_g, \quad (g=1, \dots, r)$$

$$= \sum_{\psi(D) \psi(G)=1} f(D) f(G)$$

$$= \left\{ \sum_{\psi(D)=1} f(D) \right\} \times \left\{ \sum_{\psi(G)=1} f(G) \right\} \quad (g=1, 2, \dots, r)$$

$$\prod_{i=1}^s d_{ig} = M_g \quad \prod_{i=1}^s \delta_{ig} = N_g$$

$$= F(M_1, \dots, M_r) \times F(N_1, \dots, N_r)$$

so that F is multiplicative.

2. The following are some other particular cases of the generalized composition.

(1) Let $g(M_1, \dots, M_r)$ denote the g.c.d. of M_1, \dots, M_r , and define $\psi \left(\frac{M_1, \dots, M_r}{N_1, \dots, N_r} \right)$ to be $g(M_1, \dots, M_r) \times E(N_1, \dots, N_r)$. Then ψ is clearly multiplicative. Therefore

$$\sum_{g(d_1, \dots, d_r)=1; d_i | M_i} f \left(\frac{d_1, \dots, d_r}{M_1/d_1, \dots, M_r/d_r} \right)$$

is multiplicative if f is multiplicative.

(2) Take ψ to be $\prod_{i \neq g} g(M_i, M_g) E(N_1, \dots, N_r)$. Then the multiplicativity of F follows that of f .

(3) Take $\psi \left(\frac{M_1, \dots, M_r}{N_1, \dots, N_r} \right)$ to be

$$\prod_{i=1}^r g(M_i, m_i) E(N_1, \dots, N_r)$$

where m_i ($i = 1, \dots, r$) are given numbers. Then ψ is multiplicative. Therefore if f is multiplicative so also is the function

$$\sum_{\substack{g(d_i, m_i)=1 \\ (d_i | M_i; i=1, \dots, r)}} f \left(\frac{d_1, \dots, d_r}{M_1/d_1, \dots, M_r/d_r} \right).$$

(4) Let $\psi \left(\frac{M_1, \dots, M_r}{N_1, \dots, N_r} \right)$ be $g(M_1, \dots, M_r, N_1, \dots, N_r)$; then we see that if f be multiplicative

$$\sum_{g(d_1, \dots, d_r, M_1/d_1, \dots, M_r/d_r)=1, d_i | M_i} f \left(\frac{d_1, \dots, d_r}{M_1/d_1, \dots, M_r/d_r} \right)$$

is also multiplicative.

3. *Principal functions.*— f is called a principal function of r arguments equivalent to θ if

$$f(M_1, \dots, M_r) = 0, \text{ unless } M_1 = \dots = M_r,$$

$$\text{and } f(M, \dots, M) = \theta(M).$$

We shall write $f = \text{princ } \theta$.

THEOREM 2: If f_1, f_2 be two principal functions of r arguments equivalent to θ_1 and θ_2 respectively, then

$$f_1 \cdot f_2 = \text{princ } \theta_1 \cdot \text{princ } \theta_2 = \text{princ } (\theta_1 \cdot \theta_2),$$

and

$$f_1 \oplus f_2 = \text{princ } \theta_1 \oplus \text{princ } \theta_2 = \text{princ } (\theta_1 \oplus \theta_2).$$

All terms in the sum

$$\sum f_1(d_1, \dots, d_r) f_2\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right)$$

where the summation is for any set of divisors d_i of M_i ($i = 1, \dots, r$) will vanish unless

$$d_1 = d_2 = \dots = d_r, \quad \frac{M_1}{d_1} = \dots = \frac{M_r}{d_r}$$

simultaneously, and so it is a principal function. In particular it follows that the composite or the compound of two principal functions is a principal function.

Also

$$\begin{aligned} (\text{princ } \theta_1 \cdot \text{princ } \theta_2)(M, \dots, M) &= \sum_{d|M} f_1(d_1, \dots, d) f_2\left(\frac{M}{d}, \dots, \frac{M}{d}\right) \\ &= \sum_{d|M} \theta_1(d) \theta_2\left(\frac{M}{d}\right) = (\theta_1 \cdot \theta_2)(M); \end{aligned}$$

and

$$\begin{aligned} (\text{princ } \theta_1 \oplus \text{princ } \theta_2)(M, \dots, M) &= \sum_{d|M; g(d, M/d)=1} f_1(d, \dots, d) f_2\left(\frac{M}{d}, \dots, \frac{M}{d}\right) \\ &= \sum_{d|M; g(d, M/d)=1} \theta_1(d) \theta_2(M/d) = (\theta_1 \oplus \theta_2)(M); \end{aligned}$$

whence the required results follow.

THEOREM 3: The function

$$\sum f\left(\frac{M_1}{d}, \dots, \frac{M_r}{d}\right) \theta(d)$$

where the summation is for all common divisors d of M_1, \dots, M_r is equal to

$$(f \cdot \text{princ } \theta)(M_1, \dots, M_r).$$

$$\text{For } (f \cdot \text{princ } \theta)(M_1, \dots, M_r) = \sum_{d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right) (\text{princ } \theta)(d_1, \dots, d_r)$$

$$\begin{aligned} \text{But } (\text{princ } \theta)(d_1, \dots, d_r) &= 0 \text{ unless } d_1 = \dots = d_r, \\ &= \theta(d) \text{ if } d_1 = \dots = d_r = d, \end{aligned}$$

$$\text{so that } \sum_{d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right) (\text{princ } \theta)(d_1, \dots, d_r)$$

$$= \sum f\left(\frac{M_1}{d}, \dots, \frac{M_r}{d}\right) \theta(d)$$

the summation being for all common divisors d of M_1, \dots, M_r .

In a similar manner we prove

THEOREM 4: The function

$$\sum_{d|M_1, \dots, M_r; g(d, M_i/d)=1} f\left(\frac{M_1}{d}, \dots, \frac{M_r}{d}\right) \theta(d)$$

is equal to $(f \oplus \text{princ } \theta)(M_1, \dots, M_r)$.

4. Let us write $f_1(M_1, \dots, M_r)$ for

$$\sum_{g(d_1, \dots, d_r)=1; d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right),$$

and g for $g(M_1, \dots, M_r)$. Then

$$\begin{aligned} \sum_{d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right) &= \sum_{d|g} \sum_{g(d_1, \dots, d_r)=d; d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right) \\ &= \sum_{d|g} \sum_{g(\delta_1, \dots, \delta_r)=1; \delta_i \mid \frac{M_i}{d}} f\left(\frac{M_1}{d\delta_1}, \dots, \frac{M_r}{d\delta_r}\right) \\ &= \sum_{d|g} f_1\left(\frac{M_1}{d}, \dots, \frac{M_r}{d}\right) \\ &= (f_1 \cdot \text{princ } E)(M_1, \dots, M_r), \text{ by Theorem 3.} \end{aligned}$$

Thus we get

THEOREM 5: If $f_1(M_1, \dots, M_r) = \sum_{g(d_1, \dots, d_r)=1; d_i|M_i} f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right)$, then

$$f \cdot E = f_1 \cdot \text{princ } E;$$

or, equivalently (denoting the inverse of E by E^{-1})

$$f_1 = f \cdot E \cdot \text{princ } E^{-1}$$

Corollary.—By definition* $f_1(M_1, \dots, M_r)$

$$\begin{aligned} &= \sum_{d_i|M_i} E_0(g(d_1, \dots, d_r)) f\left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}\right) \\ &= \{E_0(g) \cdot f\}(M_1, \dots, M_r), \text{ say.} \end{aligned}$$

Therefore, taking f to be E_0 we get

$$E_0\{g(M_1, \dots, M_r)\} = (E \cdot \text{princ } E^{-1})(M_1, \dots, M_r).$$

* E_0 is the function which vanishes unless all the arguments are unity and then is equal to unity.

Example.—Take f to be the function $\phi_k (M_1, \dots, M_r)$

$$= \prod_i \phi_k (M_i)$$

where $\phi_k (M)$ is the Jordan function representing the number of sets of k numbers not greater than M whose g.c.d. is prime to M . Then

$$\phi_k (M_1, \dots, M_r) = (I_k \cdot E^{-1}) (M_1, \dots, M_r)$$

where $I_k (M_1, \dots, M_r) = \prod_i I_k (M_i)$, $I_k (M) = M^k$,

and $E^{-1} (M_1, \dots, M_r) = \prod_i E^{-1} (M_i)$.

Applying Theorem 5 we get

$$\begin{aligned} \sum_{g(d_1, \dots, d_r)=1} \phi_k \left(\frac{M_1}{d_1} \right) \dots \phi_k \left(\frac{M_r}{d_r} \right) &= (I_k \cdot E^{-1} \cdot E \cdot \text{princ } E^{-1}) (M_1, \dots, M_r) \\ &= (I_k \cdot \text{princ } E^{-1}) (M_1, \dots, M_r) \\ &= \sum \left(\frac{M_1, \dots, M_r}{d^r} \right)^k \mu(d) \\ &= (M_1, \dots, M_r)^k \sum \mu(d) / d^{rk}, \end{aligned}$$

where μ is the Mobius function and the summations on the right-side are for all common divisors d of M_1, \dots, M_r .

5. Let $f(M_1, \dots, M_r)$ be the principal function equivalent to $\psi(M)$ and consider the sum

$$\sum_{g(d_1, \dots, d_r)=1; d_i | M_i} f_1(d_1, \dots, d_r) f \left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r} \right)$$

f_1 being an arbitrary function. Obviously we need consider only such divisors which make $\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r}$ equal, say, to t . Also we are to have $g(d_1, \dots, d_r) = 1$, so that it follows that t is the g.c.d. of M_1, \dots, M_r . Hence there is only one set of divisors $\left(\frac{M_1}{t}, \dots, \frac{M_r}{t} \right)$ for which the terms of the sum can be non-vanishing. Therefore we have

$$\sum_{g(d_1, \dots, d_r)=1; d_i | M_i} f_1(d_1, \dots, d_r) f \left(\frac{M_1}{d_1}, \dots, \frac{M_r}{d_r} \right) = f_1 \left(\frac{M_1}{t}, \dots, \frac{M_r}{t} \right) \psi(t)$$

Taking f_1 and ψ to be E we have

$$E_0(g) \cdot \text{princ } E = E, \text{ or } E_0(g) = E \cdot \text{princ } E^{-1}$$

which is the corollary of Th. 5.

Hence we have

THEOREM 6: If t denotes the g.c.d. of M_1, \dots, M_r , then

$$\begin{aligned} f_1\left(\frac{M_1}{t}, \dots, \frac{M_r}{t}\right) \psi(t) &= \left\{ (f_1 \times E_0(g)) \cdot \text{princ } \psi \right\} (M_1, \dots, M_r) \\ &= \left\{ (f_1 \times (E \cdot \text{princ } E^{-1})) \cdot \text{princ } \psi \right\} (M_1, \dots, M_r). \end{aligned}$$

Taking $f_1 = E$ we get

$$\begin{aligned} \psi \{g(M_1, \dots, M_r)\} &= (E \cdot \text{princ } E^{-1} \psi) (M_1, \dots, M_r) \\ &= [E \cdot \text{princ } (\psi \cdot E^{-1})] (M_1, \dots, M_r). \end{aligned}$$

Thus we have

THEOREM 7*: If $f(M_1, \dots, M_r)$ be a function $\psi(t)$ of the g.c.d. t of M_1, \dots, M_r , then it is the integral of the principal function equivalent to the function whose integral is ψ .

Taking ψ to be E in Theorem 6 we get

THEOREM 8: If t is the g.c.d. of M_1, \dots, M_r , then

$$f_1\left(\frac{M_1}{t}, \dots, \frac{M_r}{t}\right) = \left\{ (f \times (E \cdot \text{princ } E^{-1})) \cdot \text{princ } E \right\} (M_1, \dots, M_r).$$

Analogous to Theorem 6 we can easily obtain

THEOREM 9: If t is the g.c.d. of M_1, \dots, M_r , then

$$\begin{aligned} &\left\{ (f_1 \times E_0(g)) \oplus \text{princ } \psi \right\} (M_1, \dots, M_r) \\ &= f_1\left(\frac{M_1}{t}, \dots, \frac{M_r}{t}\right) \psi(t), \text{ if } g\left(t, \frac{M_i}{t}\right) = 1 \\ &= 0, \text{ otherwise.} \end{aligned}$$

6. We shall require the following considerations in Section 3.

Let $P(a_1, \dots, a_r; M)$ denote the number of solutions in non-zero positive integers of the equation

$$a_1 x_1 + \dots + a_r x_r = M,$$

the a 's and M being positive integers, the g.c.d. of x_1, \dots, x_r being unity. Consider the function

$$\theta(M) = \sum_{a_1 M_1 + \dots + a_r M_r = M} f\{g(M_1, \dots, M_r)\}.$$

Let $g(M_1, \dots, M_r) = d$. Then d is also a divisor of M .

* This result, when f is multiplicative, is the theorem of R. Vaidyanathaswamy mentioned in the Introduction.

It is therefore clear that we may write

$$\begin{aligned}\theta(M) &= \sum_{\substack{d|M \\ g(N_1, \dots, N_r)=1}} \sum_{a_1 N_1 + \dots + a_r N_r = M/d} f(d) \\ &= \sum_{d|M} f(d) P(a_1, \dots, a_r; M/d).\end{aligned}$$

This relation may also be written in the form

$$(\theta \cdot f^{-1})(M) = P(a_1, \dots, a_r; M),$$

provided $f(1) \neq 0$.

Section 2. Multiple Dirichlet Series.

1. A series of the form

$$\sum_{M_i=1; i=1, \dots, r}^{\infty} f(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r})$$

shall be called a multiple Dirichlet series. In all cases under consideration we shall suppose that s_1, \dots, s_r are so chosen as to ensure the absolute convergence of the series.

Let $\sum f_1(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r})$,

$$\sum f_2(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r})$$

be two multiple Dirichlet series. Then it can readily be shown that their product is the series

$$\sum (f_1 \cdot f_2)(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r}).$$

Let f_2 be the principal function equivalent to ψ . Then

$$\sum f_2(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r}) = \sum \psi(M)/M^{s_1 + \dots + s_r}.$$

It follows that

$$\begin{aligned}&\{\sum f_1(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r})\} \{\sum \psi(M)/M^{s_1 + \dots + s_r}\} \\ &= \sum \left\{ \sum f_1\left(\frac{M_1}{d}, \dots, \frac{M_r}{d}\right) \psi(d) \right\} / (M_1^{s_1} \dots M_r^{s_r})\end{aligned}$$

where \sum_d denotes summation for all common divisors d of M_1, \dots, M_r .

2. Now $\sum_{g(M_1, \dots, M_r)=1} 1/(M_1^{s_1}, \dots, M_r^{s_r})$

$$\begin{aligned}&= \sum E_0 [g(M_1, \dots, M_r)]/(M_1^{s_1} \dots M_r^{s_r}) \\ &= \sum (E \cdot \text{princ } E^{-1})(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r}) \\ &= \{\sum E(M_1, \dots, M_r)/(M_1^{s_1}, \dots, M_r^{s_r})\} \sum \mu(M)/M^{s_1 + \dots + s_r} \\ &= \left\{ \prod_{i=1}^r \zeta(s_i) \right\} / \zeta(\sum s_i),\end{aligned}$$

where $\zeta(s)$ is the Riemann Zeta function $\sum \frac{1}{n^s}$.

Since $\psi [g (M_1, \dots, M_r)] = [E_0 (g) \cdot \text{princ } \psi] (M_1, \dots, M_r)$
we have also

$$\begin{aligned} & [\{\Pi \zeta (s_i)\} / \zeta (\Sigma s_i)] \times \Sigma \psi (M) / M^{s_1 + \dots + s_r} \\ & = \Sigma \psi [g (M_1, \dots, M_r)] / (M_1^{s_1}, \dots, \end{aligned}$$

Examples.—(1) Put $\psi = \mu (M)$. Then we get

$$\Sigma \mu (g (M_1, \dots, M_r)) / (M_1^{s_1}, \dots, M_r^{s_r}) = \{\Pi \zeta (s_i)\} / \{\zeta (\Sigma s_i)\}^2,$$

(2) Put $\psi =$ the Jordan function ϕ_k . Then

$$\begin{aligned} \Sigma \phi_k (g (M_1, \dots, M_r)) / (M_1^{s_1}, \dots, M_r^{s_r}) &= \frac{\Pi \zeta (s_i)}{\zeta (\Sigma s_i)} \times \frac{\zeta (\Sigma s_i - k)}{\Pi \zeta (s_i)} \\ &= \zeta (\Sigma s_i - k) / \zeta (\Sigma s_i). \end{aligned}$$

(3) Put $\psi (M) = \sigma_a (M)$ representing the sum of the a th powers of the divisors of M . Then

$$\begin{aligned} \Sigma \sigma_a (g (M_1, \dots, M_r)) / (M_1^{s_1}, \dots, M_r^{s_r}) &= \frac{\Pi \zeta (s_i)}{\zeta (\Sigma s_i)} \times \zeta (\Sigma s_i) \zeta (\Sigma s_i - a) \\ &= \{\Pi \zeta (s_i)\} \zeta (\Sigma s_i - a). \end{aligned}$$

(4) Put $\psi (M) = \sigma_a (M) \sigma_b (M)$. Then

$$\begin{aligned} & \Sigma \sigma_a (g (M_1, \dots, M_r)) \sigma_b (g (M_1, \dots, M_r)) / (M_1^{s_1}, \dots, M_r^{s_r}) \\ &= \frac{\Pi \zeta (s_i)}{\zeta (\Sigma s_i)} \times \frac{\zeta (\Sigma s_i) \zeta (\Sigma s_i - a) \zeta (\Sigma s_i - b) \zeta (\Sigma s_i - a - b)}{\zeta (2 \Sigma s_i - a - b)} \\ &= \{\Pi \zeta (s_i)\} \zeta (\Sigma s_i - a) \zeta (\Sigma s_i - b) \zeta (\Sigma s_i - a - b) / \zeta (2 \Sigma s_i - a - b). \end{aligned}$$

3. Theorem 6 of Section 1 gives

$$\psi (t) f\left(\frac{M_1}{t}, \dots, \frac{M_r}{t}\right) = \{(f \times E_0 (g)) \cdot \text{princ } \psi\} (M_1, \dots, M_r)$$

where $t = g (M_1, \dots, M_r)$.

$$\begin{aligned} & \text{Therefore, } \Sigma \psi (t) f\left(\frac{M_1}{t}, \dots, \frac{M_r}{t}\right) / (M_1^{s_1}, \dots, M_r^{s_r}) \\ &= \{\Sigma f (M_1, \dots, M_r) E_0 \{g (M_1, \dots, M_r)\} / (M_1^{s_1}, \dots, M_r^{s_r})\} \times \Sigma \psi (M) / M^{s_1 + \dots + s_r}. \end{aligned}$$

$$\begin{aligned} & \text{But } \Sigma_{g (M_1, \dots, M_r) = 1} f (M_1, \dots, M_r) / (M_1^{s_1}, \dots, M_r^{s_r}) \\ &= \Sigma f (M_1, \dots, M_r) E_0 \{g (M_1, \dots, M_r)\} / (M_1^{s_1}, \dots, M_r^{s_r}) \end{aligned}$$

$$\text{Hence we have } \Sigma \psi (t) f\left(\frac{M_1}{t}, \frac{M_2}{t}, \dots, \frac{M_r}{t}\right) / (M_1^{s_1}, \dots, M_r^{s_r})$$

$$= \{\Sigma \psi (M) / M^{s_1 + \dots + s_r}\} \times \Sigma_{g (M_1, \dots, M_r) = 1} f (M_1, \dots, M_r) / (M_1^{s_1}, \dots, M_r^{s_r}),$$

where t is the g.c.d. of M_1, \dots, M_r .

Section 3. Multiple Lambert Series.

The series $\sum_{\substack{m_i=1 \\ i=1, \dots, r}}^{\infty} f(m_1, \dots, m_r) \frac{x_1^{m_1} \dots x_r^{m_r}}{(1-x_1^{m_1}) \dots (1-x_r^{m_r})}$

shall be called a multiple Lambert series. Here again, as in the previous section we shall suppose that the series considered are absolutely convergent.

Expanding the series as a power series in x_1, \dots, x_r , we get

$$\begin{aligned} \Sigma f(m_1, \dots, m_r) \frac{x_1^{m_1} \dots x_r^{m_r}}{(1-x_1^{m_1}) \dots (1-x_r^{m_r})} \\ = \Sigma (f \cdot E)(m_1, \dots, m_r) x_1^{m_1} \dots x_r^{m_r}. \end{aligned}$$

Replacing f by $f \cdot E^{-1}$ we see that

$$\begin{aligned} \Sigma (f \cdot E^{-1})(m_1, \dots, m_r) \frac{x_1^{m_1} \dots x_r^{m_r}}{(1-x_1^{m_1}) \dots (1-x_r^{m_r})} \\ = \Sigma f(m_1, \dots, m_r) x_1^{m_1} \dots x_r^{m_r}. \end{aligned}$$

$$\begin{aligned} \text{Let } f(m_1, \dots, m_r) &= \psi \{g(m_1, \dots, m_r)\}, \\ &= \{E \cdot \text{princ}(E^{-1} \cdot \psi)\}(m_1, \dots, m_r). \end{aligned}$$

Then we get

$$\begin{aligned} \Sigma \text{princ}(E^{-1} \cdot \psi)(m_1, \dots, m_r) \frac{x_1^{m_1} \dots x_r^{m_r}}{(1-x_1^{m_1}) \dots (1-x_r^{m_r})} \\ = \Sigma \psi \{g(m_1, \dots, m_r)\} x_1^{m_1} \dots x_r^{m_r}. \end{aligned}$$

The left-side is equal to

$$\sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \frac{(x_1, \dots, x_r)^m}{(1-x_1^m) \dots (1-x_r^m)}$$

so that we have

$$\sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \frac{(x_1 \dots x_r)^m}{(1-x_1^m) \dots (1-x_r^m)} = \Sigma \psi \{g(m_1, \dots, m_r)\} x_1^{m_1} \dots x_r^{m_r}.$$

Examples.—(1) Take $\psi(m) = m^k$ so that $\psi \cdot E^{-1}$ is the Jordan function ϕ_k . Then we get

$$\sum_{m=1}^{\infty} \phi_k(m) \frac{(x_1 \dots x_r)^m}{(1-x_1^m) \dots (1-x_r^m)} = \Sigma \{g(m_1, \dots, m_r)\}^k x_1^{m_1} \dots x_r^{m_r}.$$

(2) Put $\psi = \sigma_a$, the sum of the a th powers of the divisors of the argument. Since $(\sigma_a \cdot E^{-1})(m) = m^a$ we have

$$\sum_{m=1}^{\infty} \frac{m^a (x_1 \dots x_r)^m}{(1-x_1^m) \dots (1-x_r^m)} = \Sigma \sigma_a \{g(m_1, \dots, m_r)\} x_1^{m_1} \dots x_r^{m_r}.$$

Let us put $x_1 = x^{a_1}, \dots, x_r = x^{a_r}$. Then we have

$$\sum \psi \{g(m_1, \dots, m_r)\} x^{a_1 m_1 + \dots + a_r m_r} = \sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \frac{x^{m(a_1 + \dots + a_r)}}{(1 - x^{m a_1}) \dots (1 - x^{m a_r})}$$

But the left-side is equal to

$$\begin{aligned} \sum_{m=1}^{\infty} \left\{ \sum_{a_1 m_1 + \dots + a_r m_r = m} \psi \{g(m_1, \dots, m_r)\} \right\} x^m \\ = \sum_{m=1}^{\infty} \left\{ \sum_{d|m} \psi(d) P(a_1, \dots, a_r; \frac{m}{d}) \right\} x^m \end{aligned}$$

where $P(a_1, \dots, a_r; m)$ is the number of solutions in non-zero positive integers of the equation

$$a_1 x_1 + \dots + a_r x_r = m$$

the g.c.d. of x_1, \dots, x_r being unity (see Section 1 § 6).

Thus we get

$$\sum_{m=1}^{\infty} (\psi \cdot P)(m) x^m = \sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \frac{x^{m(a_1 + \dots + a_r)}}{(1 - x^{m a_1}) \dots (1 - x^{m a_r})}.$$

Examples.—(1) Put $\psi = E$. Then we find

$$\sum_{m=1}^{\infty} \left\{ \sum_{d|m} P(a_1, \dots, a_r; d) \right\} x^m = \frac{x^{a_1 + \dots + a_r}}{(1 - x^{a_1}) \dots (1 - x^{a_r})}.$$

(2) Put $\psi = E_0$. Then

$$\sum_{m=1}^{\infty} P(a_1, \dots, a_r; m) x^m = \sum_{m=1}^{\infty} \mu(m) \frac{x^{m(a_1 + \dots + a_r)}}{(1 - x^{m a_1}) \dots (1 - x^{m a_r})}.$$

(3) Put $\psi(m) = m^k$. Then

$$\sum_{m=1}^{\infty} \left\{ m^k \sum_{d|m} P(a_1, \dots, a_r; d/d^k) \right\} x^m = \sum \frac{\phi_k(m) x^{m(a_1 + \dots + a_r)}}{(1 - x^{m a_1}) \dots (1 - x^{m a_r})}.$$

In particular if we put $a_1 = \dots = a_r = 1$, and write

$$P(1, \dots, 1; m) = P_r(m),$$

we have

$$\begin{aligned} \sum_{m=1}^{\infty} \sum_{m_1 + \dots + m_r = m} \psi \{g(m_1, \dots, m_r)\} x^m &= \sum_{m=1}^{\infty} (\psi \cdot P_r)(m) x^m \\ &= \sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \left(\frac{x^m}{1 - x^m} \right)^r. \end{aligned}$$

Equating coefficient of x^m we get

$$\begin{aligned} \sum_{\substack{m_1 + \dots + m_r = m \\ m_i \geq 1}} \psi \{g(m_1, \dots, m_r)\} &= \sum_{d|m} \psi \left(\frac{m}{d} \right) P_r(d) \\ &= \sum_{d|m} \binom{d-1}{r-1} (\psi \cdot E^{-1}) \left(\frac{m}{d} \right), \end{aligned}$$

where $\binom{n}{r}$ denotes $n(n-1) \dots (n-r+1)/r!$

In particular $\sum_{d|m} P_r(d) = \binom{m-1}{r-1}$,

i.e.,
$$P_r(m) = \sum_{d|m} \binom{d-1}{r-1} \mu \left(\frac{m}{d} \right);$$

and
$$m^k \sum_{d|m} P_r(d)/d^k = \sum_{d|m} \binom{d-1}{r-1} \phi_k \left(\frac{m}{d} \right).$$

Let the series $\sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m)/m^r$ be absolutely convergent. Then as x tends to 1,

$$\sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m) \left(\frac{x^m}{1-x^m} \right)^r \sim \left\{ \sum_{m=1}^{\infty} (\psi \cdot E^{-1})(m)/m^r \right\} (1-x)^{-r}.$$

Therefore, if we denote

$$\begin{aligned} \sum_{m_1 + \dots + m_r = m} \psi \{g(m_1, \dots, m_r)\} &\text{ by } \Psi(m), \text{ we have} \\ \sum_{m \leq n} \Psi(m) &\sim \frac{n^r}{\Gamma(r+1)} \times \sum (\psi \cdot E^{-1})(m)/m^{r*} \\ &= \frac{n^r}{\zeta(r) \Gamma(r+1)} \sum_{m=1}^{\infty} \psi(m)/m^r. \end{aligned}$$

REFERENCES

1. R. Vaidyanathaswamy .. "The Theory of Multiplicative Arithmetic Functions," *Trans. Amer. Math. Soc.*, 1931.
2. Titchmarsh .. *Theory of Functions*.

* See Titchmarsh, *Theory of Functions*, p. 242.

BACTERIAL CHEMOTHERAPY, I : SYNTHESIS OF N¹-SUBSTITUTED SULPHANILAMIDES*

BY S. RAJAGOPALAN

(From the Haffkine Institute, Bombay)

Received April 30, 1943

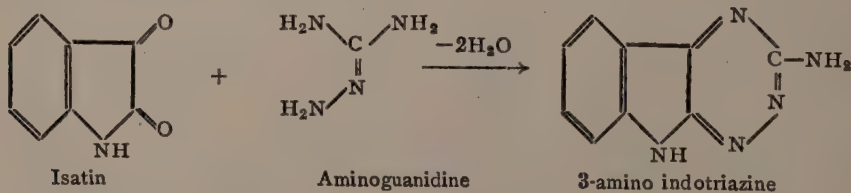
(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.Sc.)

SYSTEMATIC syntheses in the sulphanilamide group in progress at this Institute have as their objective the discovering of hitherto unknown compounds which may be of even greater therapeutic usefulness or devoid of the deleterious effects of those drugs already in clinical usage and the collection of useful information leading to an extension of our present stock of knowledge on the mode of action of these drugs which would ultimately enable the rational evolution of more powerful members of the sulphonamide group.

The view is widely held that compounds with a higher degree or greater range of therapeutic activity than sulphanilamide should be sought among its derivatives with cyclic, particularly heterocyclic, substituents at the sulphonamide radical. The present communication is a further extension of the systematic work undertaken² to synthesise the above class of compounds with all feasible ring structures and study their physiological activity in relation to their chemical constitution.

The N¹-substituted sulphanilamides (Nos. 14-23) that were synthesised in this connection are listed in Table I.

The requisite starting amines were obtained by the methods reported in literature with few modifications, the only exception being 3-amino indotriazine, necessary for the preparation of the corresponding sulphonamide (No. 23). The procedure of De and Datta⁴ was adopted for the synthesis in good yield of 3-amino indotriazine by condensation of isatin with amino guanidine in glacial acetic acid:



* A preliminary note covering part of the material presented in this communication appeared in *Current Science*.¹

TABLE I

Serial No.	Name	M.P./°C.	Nitrogen percentage	
			Found	Required
14	4-Sulphanilamido acetophenone*	189-90	9.4	9.7
15	<i>ω</i> -Sulphanilamido acetophenone	176-77 dec.	9.5	9.7
	<i>ω</i> -Sulphanilamido acetophenone hydrochloride	200-02 dec.
16	<i>ω</i> -(N ⁴ , Acetylsulphanilamido) acetophenone	151-52 dec.
	<i>ω</i> -Sulphanilamido acetonaphthone	169	8.1	8.2
	<i>ω</i> -Sulphanilamido, <i>α</i> -acetonaphthone hydrochloride	189 dec., sintg. 185
	<i>ω</i> -(N ⁴ , Acetyl sulphanilamido) acetonaphthone	2021-04 dec.
17	N ⁴ -Acetyl sulphanilamido guanidine	117-18 dec.	25.4	25.9
18	3, N ⁴ -Acetyl sulphanilamido, 1 : 2 : 4 - triazole	210 dec.	25.1	24.9
19	5-Sulphanilamido benzotriazole	135-37	24.0	24.2
20	5-Sulphanilamido indazole	243-44 dec.	19.2	19.4
	5-(N ⁴ , Acetyl sulphanilamido) indazole	262 dec.
21	7-Sulphanilamido indazole	249-50 dec.	19.3	19.4
22	1-Sulphanilyl indole	159 dec.	10.1	10.3
	1-(N ⁴ , Acetyl sulphanilyl) indole	146-47	9.0	9.0
23	3-Sulphanilamido indotriazine	200-01 dec.	24.2	24.7
	3-(N ⁴ , Acetyl sulphanilamido) indotriazine	261-62 dec.
36	<i>m</i> -Hydroxy benzylidene sulphanilamide	138	10.3	10.1
37	<i>o</i> -Nitrobenzylidene sulphanilamide	indef.	13.5	13.8
38	<i>o</i> -Nitrobenzylidene sulphanilamide	indef.	14.0	14.4
39	<i>m</i> -Nitrobenzylidene sulphathiazole	220-22 dec.	13.9	14.4

* Literature³ gives the melting point 208°C.

The amino bodies were condensed severally with crystallised acetyl sulphanilyl chloride in pyridine medium and the resulting N⁴-acetyl sulphanilamide derivatives subjected to the hydrolytic action of hot dilute hydrochloric acid, with one exception, namely, No. 22, which was obtained by hydrolysis of its N⁴-acetyl derivative with hot dilute (10 parts of 10 per cent. sodium hydroxide. Except in the case of the N⁴-acetyl derivatives of guanidine (No. 17) and triazole (No. 18), where the attempts to isolate the final compounds were not met with success, hydrolysis to the sulphonamides proceeded smoothly.

Examination of the Schiff's bases derived from the sulphonamides, as also those of the sulphones, has disclosed that while most of them are as active as the parent compounds themselves, at least in experimental streptococcal infections, a few of them were remarkably much less toxic.^{5, 11} These compounds are chemically rather unstable and their activity is conceived^{5, 6, 12} to be due to their cleavage into the original sulphonamides, on oral administration. While this mechanism of action holds for most members of this group, there are a few instances for which this explanation would not appear

acceptable without further modification. Thus, for example, *p*-hydroxy benzylidene sulphanilamide^{7, 8} is said to be more active than sulphanilamide itself. Again, the high activities claimed for the N⁴-*p*, nitrobenzylidene sulphonamides^{9, 10, 11} are noteworthy. It is also of interest that both *o*-nitrobenzylidene and *m*-hydroxy benzylidene sulphapyridines^{8, 9, 11} should be rated superior to sulphapyridine or sulphanilamide against streptococci, but inferior to sulphapyridine against pneumococci. The results with the sulphapyridine derivatives are remarkable: while a decreased activity towards the pneumococcus is conceivable, it is difficult to understand how sulphapyridine, if it is the active agent, could give an *increased* activity against streptococci, when administered as compounds which liberate it in the body. However, if these results are true, the only explanation that could be advanced would be that the "aldehyde half" of the molecule or its derivative elaborated *in vivo* exerts a modifying action on the chemotherapeutic efficacy of the "active half". The Schiff's bases (Nos. 36-39) shown in the table, besides a few others already reported in literature, were therefore prepared in order to investigate in some detail the mechanism of action of Schiff's bases derived from the sulphonamides.

The compounds reported herein are being investigated as to their usefulness in experimental bacterial infections with particular reference to plague in mice at this Institute.

Experimental

The synthesis of the final sulphonamides having been effected according to the customary procedures, the experimental details have been omitted.

3-Amino indotriazine.—A mixture of aminoguanidine carbonate (2.74 gm.) and isatin (2.94 gm., 1 mol.) in glacial acetic acid (100, c.c.) was gently refluxed for one half hour, diluted with water and basified with excess of ammonia. The 3-amino indotriazine recrystallised from alcohol as yellow needles, melting at 195-96°; yield-4.5 gm. (Found: N, 37.3; C₉H₇N₅ requires N, 37.8 %.)

The *Schiff's bases* (Nos. 36-39) were prepared by boiling together alcoholic solutions of molecular proportions of the appropriate aldehyde and the sulphonamide until crystal-separation occurred. The reaction mixture was cooled, the separated solid filtered and washed free of any traces of unreacted initial compounds by means of alcohol. These could not be recrystallised from solvents owing to their instability; they consisted of pale plates.

Except Nos. 17 and 18, the sulphonamides (Nos. 14-16, 19-23) were all recrystallised from alcohol; Nos 17 and 18 were obtained from water, all of

them (Nos. 14–22) were obtained as characteristic colourless needles, the exception being No. 18 which formed colourless prisms. The indotriazine derivative consisted of yellow needles.

The yields of all the compounds were good.

The author's grateful thanks are due to Lt.-Col. Sokhey for his kind interest and the Lady Tata Memorial Trust for the award of a Research Scholarship.

Summary

With the object of ascertaining the relative antibacterial merits of sulphonamides derived, among a few others, chiefly from heterocyclic ring systems, a series of N¹-substituted sulphonamides containing the triazole, benzotriazole, indazole, indole, and indotriazine rings have been synthesised. Additional compounds reported are the sulphonamide derivatives of acetophenone and guanidine.

A few Schiff's bases derived from the sulphonamides have also been prepared for their possible therapeutic usefulness and for a study of the mode of action of the sulphonamido Schiff's bases in general.

REFERENCES

1. Rajagopalan .. *Curr. Sci.*, 1942, **11**, 146.
2. ——— and Ganapathi .. *Proc. Ind. Acad. Sci.*, 1942, **15**, 432.
3. Merck .. *Fr.*, 1939, 847, 244 ; *C.A.*, 1941, **35**, 5513.
4. De and Dutta .. *Ber.*, 1931, **64**, 2604.
5. Henry and Gray .. *Br.*, 419, 265.
- Buttle *et al.* .. *Biochem. J.*, 1937, **31**, 724.; 1938, **32**, 1101.
- Fourneau *et al.* .. *Compt. rend. soc. biol.*, 1937, **205**, 299.
- Kolloff and Hunter .. *J. Amer. Chem. Soc.*, 1940, **62**, 1647.
6. Molitor and Robinson .. *J. Pharm. Exp. Therap.*, 1939, **65**, 405.
7. Goissedet *et al.* .. *Compt. rend. soc. biol.*, 1936, **12**, 1082.
- and Despois .. *Br.*, 1937, 456, 914.
8. Northey .. *Chem. Revs.*, 1940, **27**, 85.
9. Kolloff and Hunter .. *loc. cit.*
10. Chinoin Gyógyszer és Vegyeszeti Termékek Gyára .. *C.A.*, 1939, **33**, 7315, 7963.
11. Kolloff and Hunter .. *J. Amer. Chem. Soc.*, 1940, **62**, 159.
12. Marshall .. *Ann. Rev. Physiol.*, 1941, **3**, 643.

BACTERIAL CHEMOTHERAPY, II : SYNTHESIS OF POSSIBLE INTESTINAL ANTISEPTICS OF THE SULPHANILAMIDE GROUP

BY S. RAJAGOPALAN

(From the Haffkine Institute, Bombay)

Received April 30, 1943

(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.Sc.)

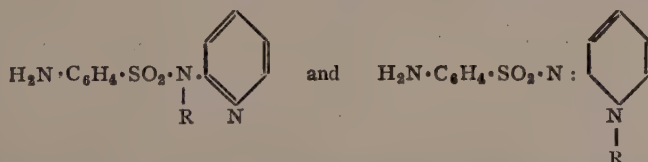
THE successful application of the sulphonamides to the chemotherapy of many types of bacterial infections led to their trial in infections of the Cholera-dysentery-typhoid group, which are characterised by their main or entire localisation in the intestinal tract. The prerequisites of a compound to be an ideal intestinal antiseptic are that it should be poorly absorbed and also possess a strong bacteriostatic and bactericidal local action. The properties of such a compound would permit the attainment of a high concentration in the intestine without being too toxic, due to a low concentration in the blood and tissues. Sulphaguanidine, a drug fulfilling these specifications, has been introduced by Marshall *et al.*¹ and heralds an advance in intestinal antiseptics. Although sulphapyridine and sulphathiazole were found on clinical trial to have some curative value in bacillary dysentery, these drugs have the disadvantage, as far as intestinal infections are concerned, of being readily absorbed from the bowels and perhaps of being renal irritants in dehydrated patients. However, the evolution of succinyl sulphathiazole²—a drug which is believed to owe its activity to its slow cleavage into sulphathiazole in the intestine—should be considered a right step in this direction.

Three compounds of the sulphonamide group—sulphathiazoline, sulphapyridine and sulphathiazole—were therefore chosen for further synthetic elaboration and study of the resulting products as to their usefulness in intestinal as well as a few other bacterial infections. It appeared that by introducing substituents at the sulphonamide part of the molecules of the sulphonamido heterocycles, compounds insoluble in alkali and therefore unlikely to be absorbed from the intestine, which is alkaline in pH, could be obtained. A list of some of the compounds prepared with this object are listed.

Serial No.	Name	M.P./°C.	Nitrogen percentage	
			Found	Required
27	3-Methyl, 2-sulphanilimido, 2 : 3-dihydro-thiazoline	196-98	15.4	15.5
28	3-Ethyl, 2-sulphanilimido, 2 : 3-dihydro-thiazoline	181-82 dec.	14.6	14.7
29	N ¹ -Phenyl sulphathiazoline	glassy liquid at 156, which clears at ca. 185	12.6	12.6
30	N ⁴ -Acetyl, N ¹ -phenyl sulphathiazoline	230 —	13.8	14.1
	N ¹ -Allyl sulphathiazoline	186-89, softg. 187		
32	N ⁴ -Acetyl, N ¹ -allyl sulphathiazoline	179-81, sintg. 176	14.4	14.6
	1- <i>p</i> , Nitrobenzyl, 2-sulphanilimido, 1 : 2-dihydro pyridine	234 dec.		
33	1- <i>p</i> , Nitrobenzyl-2-acetyl sulphanilimido, 1 : 2-dihydropyridine	215-18
	1- <i>p</i> , Nitrobenzyl-2-(<i>p</i> , nitrobenzylamino)-benzene sulphonilimido, 1 : 2-dihydro-pyridine	208-10	13.3	13.3
34	3- <i>p</i> , Nitrobenzyl-2-sulphanilimido, 2 : 3-dihydrothiazole	199-200 dec.	13.8	14.4
35	3- <i>m</i> , Nitrophenacyl-2-sulphanilimido, 2 : 3-dihydrothiazole	238-39	13.4	13.4
	3- <i>m</i> , Nitrophenacyl-2-acetyl-sulphanilimido, 2 : 3-dihydrothiazole	216-18

The nitro aralkyl derivatives (Nos. 32-35) were selected because of the high activities reported for a somewhat similar compound, N,⁴ 4'-nitrobenzyl sulphanilamide.³

There are two alternative structures possible for the compounds obtained by the above kind of operation on the sulphonamides. Taking the example of one of the sulphonamido heterocycles, namely, sulphapyridine, the introduction of an alkyl radical (R) can furnish the following isomeric products.



The production of one or other of the isomeric forms are conditioned by the experimental technique adopted and have recently been well investigated. The nomenclature adopted for the compounds reported herein are, therefore, in accordance with these studies.^{4,5}

Experimental

3-Methyl- and 3-ethyl, 2-sulphanilimido, 2 : 3-dihydrothiazolines (Nos. 27 and 28) were obtained by the action of a slight excess of the appropriate alkyl

sulphate or iodide on an aqueous alkaline solution of sulphathiazoline. They consisted of colourless needles or plates after crystallisation from alcohol.

*N*¹-Phenyl sulphathiazoline (No. 29): 2-Anilino thiazoline.—The method available in literature⁶ gave only a poor yield of this compound. A modified procedure afforded the desired amine in a very much better yield; a mixture of β -bromoethylamine hydrobromide (10 gm.) in water and phenyl isothiocyanate (6.7 gm., 1 mol.) was cooled and treated with excess of 20 per cent. sodium hydroxide. The separated crystals were purified through a dilute hydrochloric acid solution and separated from alcohol in colourless needles, m.p. 158–60°.

*N*¹-Phenyl sulphathiazoline was prepared by the acid hydrolysis of its *N*⁴-acetyl derivative, in turn obtained by condensation of acetyl sulphanilyl chloride with anilino thiazoline in pyridine according to general procedure.

*N*¹-Allyl sulphathiazoline (No. 30): 2-Allylamino thiazoline, prepared by the same procedure as adopted for 2-anilino thiazoline, was obtained as an oil which was used as such without further purification.

The sulphonamide (No. 30) was prepared as usual from the above amine.

1-*p*, Nitrobenzyl-2-(*p*, nitrobenzylamino-) benzene sulphonimido, 1 : 2-dihydro pyridine.—A mixture of equimolecular amounts of sodium sulphapyridine and *p*-nitrobenzyl bromide in alcohol was refluxed until a neutral reaction resulted. The desired compound, which is insoluble in both dilute hydrochloric acid and sodium hydroxide, was separated from the accompanying basic monosubstitution product (No. 32) and from unreacted sulphapyridine.

The compounds (Nos. 32, 34, 35) were obtained by the acid hydrolysis of the corresponding *N*⁴-acetyl derivatives, which in their turn were prepared by the interaction of the respective *N*¹-sodio sulphonamides and the appropriate alkyl bromides in alcoholic solution.

The nitro compounds (Nos. 32–35) were obtained as yellow crystals from pyridine.

The author desires to express his gratefulness to Lt.—Col. Sokhey for his keen interest and encouragement and to the Lady Tata Memorial Trust for the award of a Scholarship.

Summary

Chiefly by the action of alkyl or aralkyl halides or the alkyl sulphates on the sulphanilamido heterocycles, a series of compounds, insoluble in alkali, has been obtained. Because of the likelihood of these not being absorbed from the intestine, which is alkaline in pH, the type of compounds synthesised are expected to prove particularly useful in infections of the intestinal tract.

REFERENCES

1. Marshall *et al.* .. *Bull. Johns. Hopkins Hosp.*, 1940, **67**, 163 ;
1941, **68**, 94.
2. Moore and Miller .. *J. Amer. Chem. Soc.*, 1942, **64**, 1572.
Poth *et al.* .. *Proc. Soc. Exp. Biol. Med.*, 1941, **48**, 129 ;
Arch. Surg., 1942, **44**, 187, 208.
3. Mayer and Oechslin .. *Arch. int. pharmacodyn.*, 1939, **62**, 21.
Northey .. *Chem. Revs.*, 1940, **27**, 118.
4. Druey .. *Helv. Chim. Acta*, 1941, **24**, 226.
Jensen .. *Ibid.*, 1941, **24**, 1219.
Shepherd *et al.* .. *J. Amer. Chem. Soc.*, 1942, **64**, 2532.
5. Ganapathi .. *Private communication.*
6. Menne .. *Ber.*, 1900, **33**, 659.

BACTERIAL CHEMOTHERAPY, III: SYNTHESIS OF POSSIBLE LIPOPHILIC CHEMOTHERAPEUTICALS OF THE SULPHANILAMIDE GROUP*

BY S. RAJAGOPALAN

(From the Haffkine Institute, Bombay)

Received April 30, 1943

(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.Sc.)

ALTHOUGH the compounds of the sulphanilamide group already evolved have provided medical science with some of the most potent weapons for the effective conquest of many diseases of bacterial origin, there is still a long list of bacterial infections uninfluenced by the newer chemotherapeutics; among the latter, leprosy and tuberculosis continue to constitute the major posers to chemotherapy. This justifies further exploratory work both on compounds closely related to the effective substances already known and on their structural allies but with other substituents. The present study is one of a series of such exploratory investigations in the sulphanilamide group undertaken at this Institute with the object of extending their range of therapeutic usefulness in bacterial infections, also including those caused by the acid-fast mycobacterium.

The newer reports of the effectiveness of the treatment of experimental tuberculosis in the guinea pig and the rabbit with members of the sulphanilamide group are still discordant. A number of workers have claimed that sulphanilamide,^{2, 3} sulphapyridine,⁴ prontosil soluble,⁵ sulphathiazole^{6, 7} and sulphadiazine⁷ in high blood-levels may modify the course of experimental tuberculosis. However the results obtained so far do not appear to warrant clinical trial of any of the aforementioned compounds. The low antitubercular activity of the sulphonamides, notwithstanding their direct action on many pathogenic organisms,⁸ has been put down as perhaps partly due to their inability to penetrate the lipid layer of the bacteria. Consequently, an attempt has been made to achieve better results by introducing lipophilic radicals into the sulphonamides. On this basis, only a single compound, N¹-dodecanoyl sulphanilamide, has been prepared⁹ and tested experimentally without, however, consistent success.^{10, 11} On the ground that sulphathiazole is more active than sulphanilamide against most bacteria, the introduction of a lipophilic substituent in the heterocyclic part of the

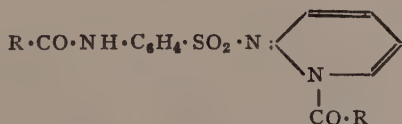
* A preliminary note covering part of the material embodied in this communication appeared in *Current Science*.¹

former has been tried; a series of alkyl sulphathiazoles¹² as well as several sulphathiodiazoles¹³ have been prepared but have not yet been tested against the tubercle bacillus. Thus the results secured so far can in no sense be called uniform.

Study of the numerous acyl derivatives of the sulphonamides hitherto synthesised has disclosed a few members effective in combating experimental coccal infections in mice associated with a low order of toxicity; some of them have also passed actual clinical trials.¹⁴ However, with the exception of N¹-dodecanoyl sulphanilamide which is uncertainly reported, on^{9, 10, 11} and the chaulmoogryl derivative¹¹ of sulphanilamide, none of the fatty acid derivatives of the sulphonamides appear to have been investigated as to their efficacy in tuberculosis or leprosy.

The present communication represents one of the many possible lines of attack for ascertaining whether or not the sulphonamides can be pressed to service in the conquest of mycobacterial infections by suitable synthetic operations on the molecule of sulphanilamide. Accordingly, a series of acyl derivatives of the sulphonamides have been synthesised in the expectation that these might exhibit a much greater ability to penetrate the lipid layer of the tubercle and lepra bacilli as compared to the parent sulphonamides. The sulphonamides chosen for necessary modifications of their molecules in order to render them lipophilic were all previously known and reported to be active at least in some coccal infections. The final sulphonamides, prepared in this connection, are represented in Table I.

For purposes of convenience, the nomenclature of Crossley, Northey and Hultquist¹⁷ has been adopted. This does not however, exclude the alternative structure



for the N⁴, N¹-diacyl sulphapyridines (Nos. 66–71 and 73) which is also possible.¹⁸ In all probability they are equilibrium mixtures of the two isomeric forms. The compounds Nos. 86–92 have been assigned the structure represented in the table on the basis of their mode of preparation and in accordance with recent studies¹⁸ on this type of compounds.

Besides the simple normal fatty acyl derivatives, a few branched-chain acyl sulphonamides (Nos. 71, 73, 79, 80, 84), of which Nos. 71, 79 and 84 contain the advantageous cyclohexyl group,¹⁹ were also included in this study in view of the interesting results obtained by Robinson and Birch²⁰ with acids of the latter type.

TABLE I

Serial No.	Name	M.P./°C.	Nitrogen percentage	
			Found	Required
40	N ⁴ - <i>n</i> , Caprylyl sulphanilamide*	198	9.6	9.7
41	N ⁴ -Cyclohexoyl sulphanilamide	238	9.8	9.9
61	N ⁴ - <i>n</i> , Butyryl sulphapyridine	206	12.9	13.2
63	N ⁴ - <i>n</i> , Heptoyl sulphapyridine	193	11.6	11.6
64	N ⁴ - <i>n</i> , Caprylyl sulphapyridine	213-14	10.8	11.2
66	N ⁴ , N ¹ -Diacetyl sulphapyridine	194	11.8	12.6
67	N ⁴ , N ¹ -Di (<i>n</i> , butyryl)-sulphapyridine	163	10.7	10.8
68	N ⁴ , N ¹ -Di (<i>n</i> , caproyl)-sulphapyridine	155-57	10.1	9.5
69	N ⁴ , N ¹ -Di (<i>n</i> , caprylyl)-sulphapyridine	135	8.5	8.4
70	N ⁴ , N ¹ -Dibenzoyl sulphapyridine	217	9.2	9.2
71	N ⁴ , N ¹ -Dicyclohexoyl sulphapyridine	193-95	8.6	9.0
73	N ⁴ , N ¹ -Dicinnamoyl sulphapyridine	196-98	8.6	8.3
74	N ⁴ - <i>n</i> , Butyryl sulphathiazole	244-46 dec.	12.4	12.5
75	N ⁴ - <i>n</i> , Caproyl sulphathiazole	198-99	11.2	11.6
76	N ⁴ - <i>n</i> , Heptoyl sulphathiazole	202-03	10.8	11.1
77	N ⁴ -Palmityl sulphathiazole	140-47	8.3	8.5
78	N ⁴ -Stearyl sulphathiazole	148-50	7.8	8.1
79	N ⁴ -Cyclohexoyl sulphathiazole	222-23 dec.	11.5	11.5
80	N ⁴ -Furoyl sulphathiazole	dec. above 240	12.0	12.0
81	N ⁴ - <i>n</i> , Butyryl sulphathiazoline	224-25	12.1	12.5
82	N ¹ - <i>n</i> , Caproyl sulphathiazoline	181-82	11.2	11.5
83	N ⁴ - <i>n</i> , Heptoyl sulphathiazoline	175-76	11.2	11.1
84	N ⁴ -Cyclohexoyl sulphathiazoline	220	11.5	11.4
85	N ⁴ - <i>n</i> , Caprylyl sulphanildimethylamide	79-82	8.4	8.6
86	1-Methyl, 2-(N ⁴ - <i>n</i> , butyryl sulphanilimido) 1 : 2-dihydro pyridine	213	12.6	12.6
87	1-Methyl, 2-(N ⁴ - <i>n</i> , caproyl sulphanilimido) 1 : 2-dihydro pyridine	213-15	11.8	11.6
88	3-Methyl, 2-(N ⁴ - <i>n</i> , caproyl sulphanilimido) 2 : 3-dihydro thiazole	215	11.5	11.4
89	3-Methyl, 2-(N ⁴ - <i>n</i> , heptoyl sulphanilimido) 2 : 3-dihydro thiazole	173-74	11.3	11.0
90	3-Methyl, 2-(N ⁴ - <i>n</i> , caprylyl sulphanilimido) 2 : 3-dihydro thiazole	153-54	10.4	10.6
91	3-Methyl, 2-(N ⁴ - <i>n</i> , caproyl sulphanilimido) 2 : 3-dihydro thiazoline	201-03	11.1	11.4
92	3-Methyl, 2-(N ⁴ - <i>n</i> , heptoyl sulphanilimido) 2 : 3-dihydro thiazoline	170	11.0	11.0
93	N ⁴ - <i>n</i> , Butyryl, N ¹ -(<i>p</i> -nitrophenyl)-sulphanilamide	248-50 dec.	11.2	11.6
94	N ⁴ - <i>n</i> , Caproyl, N ¹ -(<i>p</i> -nitrophenyl)-sulphanilamide†	152	10.3	10.7
95	N ⁴ - <i>n</i> , Butyryl sulphanilyl sulphanilamide	235-36	10.6	10.6
96	N ⁴ - <i>n</i> , Caproyl sulphanilyl sulphanilamide	184-86	9.4	9.9
97	2-Sulphanilamido benzoic acid‡	ca. 215 dec.	9.4	9.6
97	2-(N ⁴ - <i>n</i> , Butyryl sulphanilamido)-benzoic acid	226-28 dec.	7.3	7.7
98	4-Sulphanilamido benzoic acid§	181-82	9.3	9.6
98	4-(N ⁴ - <i>n</i> , Butyryl sulphanilamido)-benzoic acid	224-26	7.4	7.7

* Various reported¹⁵ to melt at 189° and 200°C.† Literature¹⁶ gives the m.p. 225°C.‡ Reported by Koloff²¹ to melt at 225°C.§ Koloff²¹ reports m.p. 202°C., Crossley *et al*¹⁷ give m.p. 198-200°C.

Experimental

The N⁴-acyl sulphonamides (Nos. 40, 41, 61, 63, 64, 74–84, 93–98) were prepared by condensation of molecular proportions of the requisite acid chlorides on the respective sulphonamides in the presence of pyridine. The condensation products, obtained by dilution of the reaction mixtures with excess of water, were severally purified through precipitation from their dilute sodium hydroxide solutions (decolorising carbon) by acidification with excess of dilute hydrochloric acid. They were finally recrystallised from either alcohol (Nos. 40, 41, 61, 63, 74–79, 93–98) or acetic acid (Nos. 64, 80–84) in colourless needles with the exception of Nos. 74, 75, 93 and 94, which were obtained as slightly pale plates or prismatic needles. The compound No. 97 was recrystallised from acetone in colourless needles.

Of the remaining N⁴-acyl sulphonamides, the compounds, Nos. 85, 88–90 were prepared by operation of molecular proportions of the appropriate acid chlorides on the respective sulphonamides in pyridine medium; for the remaining compounds, viz., Nos. 86, 87, 91, 92, the corresponding N⁴-acyl but N¹-unsubstituted sulphonamides constituted the starting materials: aqueous alkaline solutions of these, on methylation with dimethyl sulphate, furnished the desired compounds. The compounds were first purified and freed from traces of the initial parent sulphonamides by suitable methods dictated by their differences in character when they were obtained as well defined, colourless crystals. The compound No. 85 was crystallised from acetone; the sulphathiazole derivatives, Nos. 88, 89 and 90, were obtained from acetic acid while the rest were crystallised from alcohol.

The N⁴-N¹-disubstituted sulphapyridines (Nos. 66–71, 73) resulted directly by the operation of slightly more than 2 mols. of the appropriate acid chloride on sulphapyridine itself in pyridine solution. These products were isolated by taking advantage of their characteristic insolubility in both dilute mineral acids and alkalies. As hot polar solvents had the tendency to split off the acyl groups at the N¹-nitrogen of these compounds—in the case of the straight chain acid compounds, hot water broke them down to the corresponding N⁴-acyl derivatives and the acids, while hot alcohol readily converted them to a mixture of the respective N⁴-acyl derivatives and the acid esters—it was found advantageous to effect their recrystallisation by dilution of their solutions (charcoal) in acetone. These were then obtained as colourless plates and were dried *in vacuo* over anhydrous calcium chloride.

The yields of the final compounds reported herein, in all the instances, were good.

I am thankful to Col. S. S. Sokhey for his kind interest in this investigation and to the Lady Tata Memorial Trust for the award of a Research Scholarship.

Summary

On the ground that the sulphonamide group of drugs after suitable synthetic modifications of their molecules may probably be useful in mycobacterial infections, the possibility of rendering a few members, previously known to be active in coccal infections, lipophilic by the introduction of fatty acid residues in the latter has been explored. Accordingly, normal and branched chain acyl derivatives, thirty-seven in all, of sulphanilamide, sulphapyridine, sulphathiazole, sulphathiazoline, etc., have been synthesised.

REFERENCES

1. Rajagopalan .. *Curr. Sci.*, 1942, **11**, 394.
2. Greey *et al.* .. *Proc. Soc. Exp. Biol. Med.*, 1938, **39**, 22.
Buttle and Parish .. *Brit. Med. J.*, 1938, **2**, 776.
3. Rich and Folis .. *Bull. Johns Hopkins Hosp.*, 1938, **62**, 77 ; 1939, **65**, 466.
4. Feldman and Hinshaw .. *Proc. Staff Meet., Mayo Clin.*, 1939, **14**, 174.
5. Birkhaug .. *Brit. Med. J.*, 1939, **2**, 54.
6. Ballou *et al.* .. *Amer. Rev. Tuberc.*, 1942, **45**, 217.
7. Smith and Westfall .. *J. Pharm. Exp. Therap.*, 1942, **74**, 163.
8. Whitby .. *Lancet*, 1938, **2**, 1095.
Long *et al.* .. *J. Amer. Med. Assoc.*, 1939, **112**, 115.
Green and Bielschowsky .. *Brit. J. Exp. Path.*, 1942, **23**, 13.
9. Crossley *et al.* .. *J. Amer. Chem. Soc.*, 1939, **61**, 2950.
10. Climenko .. *Proc. Soc. Exp. Biol. Med.*, 1939, **43**, 624.
Steinbach and Duca .. *Ibid.*, 1940, **44**, 133.
Muschenheim *et al.* .. *Ibid.*, 1940, **45**, 556.
11. Arnold *et al.* .. *Ber.*, 1942, **75**, 369.
12. Jensen and Kjaer .. *Dansk. Tidskr., Farmaci*, 1942, **16**, 110.
13. Arnold .. *Ber.*, 1942, **75**, 87.
14. Richard and Henderson .. *J. Pharm. Exper. Therap.*, 1941, **73**, 170.
Welebir and Barnes .. *J. Amer. Med. Assoc.*, 1941, **117**, 2132.
Maxwell and Bazalis .. *Ibid.*, 1941, **117**, 2238.
Young *et al.* .. *J. Urol.*, 1941, **45**, 903.
Parentiss and Kanealy .. *Ibid.*, 1942, **47**, 11.
15. I. G. Farbenindustrie .. *Fr.*, 820, 546 ; *C.A.*, 1938, **32**, 2958.
Miller and Moore .. *J. Amer. Chem. Soc.*, 1939, **61**, 1198.
16. Kolloff and Hunter .. *Ibid.*, 1940, **62**, 1646.
17. Crossley *et al.* .. *Ibid.*, 1938, **60**, 2217.
18. Druey .. *Helv. Chim. Acta*, 1941, **24**, 226.
Jensen .. *Ibid.*, 1941, **24**, 1219.
Shepherd *et al.* .. *J. Amer. Chem. Soc.*, 1942, **64**, 2532.
19. Adams and co-workers .. *Ibid.*, 1927, **49**, 2934 ; 1928, **50**, 1475, 2297.
20. Robinson .. *J. Chem. Soc.*, 1940, 505.
——— and Birch .. *Ibid.*, 1942, 488.
21. Kolloff .. *J. Amer. Chem. Soc.*, 1938, **60**, 950.

NEW CONVERGENCE AND SUMMABILITY TESTS FOR FOURIER SERIES

BY K. S. K. IYENGAR

Received July 5, 1943

1. LET $f(x)$ be a periodic summable function and

$$\psi_{x_0}(t) = |f(x_0 + t) + f(x_0 - t) - 2f(x_0)|. \quad (1.1)$$

Theorem A of this note is a generalization of the FeJér-Lebesgue-Hardy theorem which (latter) is:—

$$\frac{1}{u} \int_0^u \psi_{x_0}(t) dt \rightarrow 0 \text{ as } u \rightarrow 0 \text{ implies the } (C, r) \cdot (r > 0) \cdot \text{convergence of } (1.2)$$

the Fourier series of $f(x)$ at x_0 to $f(x_0)$. [Zygmund¹, FeJér², Lebesgue³, Hardy⁴.] The subsidiary theorem B of this note discusses the relation between the various forms of the hypothesis of theorem A, and in particular their relation to the (F. L. H.) hypothesis in (1.2); and with the examples given below it in 3, establishes that the (F. L. H.) theorem is a particular case of theorem A.

Theorem C is a generalization of convergence test of the Fourier series of $f(x)$ at a point x_0 due to Hardy and Littlewood⁵ (1932), the latter test being as follows:

(1) $\psi_{x_0}(t) \log t \rightarrow 0$ $t \rightarrow 0$. (2) the Fourier coefficients of $f(x) \leq An^{-\delta}$ (1.3) ($A > 0$, $\delta > 0$). Hardy and Littlewood have established their test by using the Tauberian theorem associated with Valeron⁶ (1917) means. In a recent paper⁷ (1943) I have derived this test by proving

$$(a) \quad (1) \text{ of } (1.3) \text{ implies that } \frac{1}{\log n} \sum_{r=0}^n \frac{S_r(x_0)}{n+1-r} \rightarrow f(x_0) \text{ as } n \rightarrow \infty.$$

(b) (2) of (1.3) is exactly the Tauberian condition associated with convergence by the means in (a). Proceeding along the lines of my paper,⁷ I have derived theorem C, from theorem A and a new Tauberian theorem in another paper⁸ of mine to be published shortly. It is noteworthy that the form of theorem A permits us to replace (1) in the Hardy-Littlewood

test by the slightly broader one $(1)' \frac{1}{u} \int_0^u \psi_{x_0}(t) \operatorname{Log} t \, dt \rightarrow 0, u \rightarrow 0$

or the still broader one $(1)'' \frac{1}{\operatorname{Log} u} \int_u^{\delta} \psi_{x_0}(t) \frac{\operatorname{Log} t}{t} \, dt \rightarrow 0, u \rightarrow 0$

In 7 I have discussed particular cases of interest of A and C.

[Note.—In what follows “F.L.H. hypothesis” will stand for the condition in (1.2) namely

$$\frac{1}{u} \int_0^u \psi_{x_0}(t) \, dt \rightarrow 0 \text{ as } u \rightarrow 0 \text{ and F.L.H. theorem, the theorem of (1.2).]$$

2. *Notations and Definitions.*—The $b_n, b_n', B_n, B_n', \psi_{x_0}(t), B_t, b_t, S_n(x_0)$, are defined as follows :

(1) $b_n > 0$, (2) $b_0 \geq b_1 \geq b_2 \dots \geq b_n$;

(3) $B_n = \sum_{r=0}^n b_r$ (and $\rightarrow \infty$ as $n \rightarrow \infty$). (4) $b_t = b_{[t]}, B_t = B_{[t]}, b_n', B_n'$, etc., being restricted by the same conditions;

(5) $\psi_{x_0}(t)$ defined as in (1.1); (6) $S_n(x_0) = \frac{1}{2} a_0 + \sum_1^n (a_r \cos r x_0 + b_r \sin r x_0)$ a_r, b_r , being the Fourier coefficients of $f(x), f(x)$ being as in (1.1).

3. *Statement of theorems A and B and remarks.*—

$$\text{THEOREM A: If } \frac{1}{B_x} \cdot \int_0^x \psi_{x_0}\left(\frac{1}{t}\right) \cdot \frac{B_t}{t} \, dt \rightarrow 0 \quad (a > 0) \quad (3.1)$$

$$\text{and } \frac{1}{B_N} \cdot \sum_{n=0}^N \frac{b_n}{B_n} \cdot B_n' \text{ is bounded for all } N \quad (3.2)$$

$$\text{then } \frac{1}{B_n} \cdot \sum_0^n b_r' S_{n-r}(x_0) \rightarrow f(x_0), \text{ as } n \rightarrow \infty. \quad (3.3)$$

Particular case of A of interest is as follows :

$$\text{Let } \theta(t) = \psi_{x_0}\left(\frac{1}{t}\right) \cdot \frac{B_t}{t b_t}.$$

THEOREM A₁:

$$\text{If (a) } \theta(t) \rightarrow 0 \text{ or (b) } \frac{1}{t} \int_0^t \theta(u) \, du \rightarrow 0 \text{ as } t \rightarrow \infty \text{ then (3.3) will be true.}$$

$$(3.4)$$

[It is to be noted that (b) of (3.4) could be given in another form completely equivalent to it namely $\frac{1}{t} \int_0^t \theta \left(\frac{1}{u} \right) du \rightarrow 0$ as $t \rightarrow 0$; also it can be shewn that (3.4) (a) implies (3.4) b, and (3.4) b implies (3.1)].

Subsidiary theorem B.

If $\frac{1}{B_N} \sum_{n_0}^N \frac{b_r}{B_r} B_r'$ is bounded for all $N (\geq n_0)$ (i.e. \leq some positive k) (3.5)

then $\frac{1}{B_x} \int_a^x \psi_{x_0} \left(\frac{1}{t} \right) \frac{B_t}{t} dt \rightarrow 0$ ($a > 0$) implies

$$\frac{1}{B_x'} \int_a^x \psi_{x_0} \left(\frac{1}{t} \right) \cdot \frac{B_t'}{t} dt \rightarrow 0; \quad (3.6)$$

If (3.5) is not true (3.6) is not necessarily true. (3.7)

[Note 1.—It is to be noticed that (F. L. H.) hypothesis can be put in the equivalent form $\frac{1}{x} \int_a^x \psi_{x_0} \left(\frac{1}{t} \right) dt \rightarrow 0$ $x \rightarrow \infty$; so that from conditions in

2 about b_n , it follows from theorem B that hypothesis $\frac{1}{B_x} \int_a^x \psi_{x_0} \left(\frac{1}{t} \right) \cdot \frac{B_t}{t} dt \rightarrow 0$

implies the (F. L. H.) hypothesis and if $\frac{1}{B_N} \sum_{n_0}^N \frac{B_r}{r}$ is bounded for all $N \geq n_0$ the converse is also true; so that in this case (F. L. H.) hypothesis is equivalent to hypothesis (3.1). But the form of theorem A allows us to enlarge the field of (C, r) summability for the Fourier series of $f(x)$ at x_0 as the following example shews:—

Example 1.—Let $0 < \rho_1 < \rho_2$ and $\rho_1 + \rho_2 < 1$ and $\psi(x) = \log \log \log x$. Let $F_n = n^{\rho_2 + \rho_1 \cos \psi(n)}$ and $F_n - F_{n-1} = b_n$ for sufficiently large n , say $n \geq n_0$. b_0, b_1, b_{n_0-1} being defined suitably to suit (1) and (2) of 2. then it can be proved that (a) b_n and $B_n = \sum_0^n b_r$ satisfy (1), (2), (3) of 2, and

(b) $\frac{1}{B_N} \sum_{n_0}^N \frac{B_r}{r}$ is bounded for all $N \geq n_0$. so that from theorem A it follows

$\frac{1}{B_n} \sum_0^n b_r S_{n-r}^{\rho_2 - \rho_1}(x_0) \rightarrow f(x_0)$ if (F. L. H.) hypothesis is true. It is to be noted

that $\frac{\text{Log } B_n}{\text{Log } n}$ in this case oscillates between $\rho_1 + \rho_2$ and $\rho_2 - \rho_1$.] (3.8)

[Note 2.—Hypothesis (3.2) namely boundedness of $\frac{1}{B_N} \sum_{m_0}^n \frac{b_r}{B_r} B_r'$ implies $\frac{\text{Log } B_n}{\text{Log } B_n}$ is bounded above, in particular $\frac{1}{B_N} \sum_{r=0}^n \frac{B_r}{r}$ implies $\frac{\text{Log } B_n}{\text{Log } n}$ is bounded above for $n \geq 2$.] (3.9)

[Note 3.—The following example reveals the importance of condition (3.2) in theorem A.

Example 2.—Let $f(t)$ be an even periodic bounded summable function and let its Fourier coefficients be such that $\text{Lim sup } \frac{\bar{S}_n(0)}{\text{Log } n} > 0$ where $S_n(0) = \frac{1}{2} a_0 + \sum_1^n a_r$.

$$\text{Let } \psi(t) = \frac{f(t)}{|\text{Log } |t||} \text{ in } 0 \leq |t| \leq \delta < 1 \\ = 0 \text{ otherwise.}$$

In this case the Fe Jer theorem at $t=0$ about $\psi(t)$ is true.

Taking $b_n = \frac{1}{n+1}$ it is easy to see that $\frac{1}{B_N} \sum_{r=0}^n \frac{B_r}{r}$ in this case $\rightarrow \infty$ as $N \rightarrow \infty$.

It can be established that $\frac{\sum_0^n \frac{S_{n-r}(0)}{1+r}}{\sum_0^n \frac{1}{1+r}}$ does not converge to $\psi(0) = 0$,

$S_n(0)$ = the sum of the 1st $n+1$ Fourier coefficients of $\psi(t)$. [Incidentally this example establishes (3.7) of B, *via* A.] (3.9)

[Note 4.—In view of theorem B, it is sufficient to establish theorem A in the following form:—

\bar{A} . Hypothesis (3.1) implies $\frac{1}{B_n} \sum_0^n b_r S_{n-r}(x_0) \rightarrow f(x_0)$.] (3.10)

4. *Proof of theorem B.*—

$$\text{Let } a_n = \int_n^{n+1} \psi_{x_0} \left(\frac{1}{t} \right) dt. \quad (4.1)$$

It can be easily established that

$$\frac{1}{B_n} \cdot \int_a^{\infty} \psi_{x_0} \left(\frac{1}{t} \right) \frac{B_t}{t} dt \rightarrow 0 \text{ as } x \rightarrow \infty \text{ is completely}$$

$$\text{equivalent to } \frac{1}{B_n} \sum_{r=0}^n \frac{B_r a_r}{r} \rightarrow 0 \text{ as } n \rightarrow \infty. \quad (4.2)$$

and similarly with regard to $\frac{1}{B_{x'}} \int_a^x \psi_{x_0} \left(\frac{1}{t} \right) \frac{B_t'}{t} dt \rightarrow 0$ (4.2)

so that we will have established theorem B if we prove the following:

B. If $x_n = \frac{1}{B_n} \sum_{n_0}^n \frac{B_r a_r}{r}$, and $y_n = \frac{1}{B_n'} \sum_{n_0}^n \frac{B_r' a_r}{r}$, and $\frac{1}{B_n'} \sum_{n_0}^n \frac{b_r}{B_r} B_r'$ is bounded, then $x_n \rightarrow 0$ implies $y_n \rightarrow 0$. (4.3)

Without the boundedness condition it (4.3) is not necessarily true (4.4)

Proof of B.—From definition of x_n in \bar{B} , we have

$$a_n = n(x_n - x_{n-1}) + \frac{n b_n}{B_n} x_{n-1}$$

$$\text{and } y_n = \frac{1}{B_n'} \cdot \sum_{n_0}^n B_r' (x_r - x_{r-1}) + \frac{1}{B_n'} \cdot \sum_{n_0}^n \frac{b_r}{B_r} \cdot B_r' \cdot x_{r-1} \\ = y_{n,1} + y_{n,2}. \quad (4.5)$$

From the boundedness of $\frac{1}{B_n'} \cdot \sum_{n_0}^n \frac{b_r}{B_r} B_r'$, and $x_n \rightarrow 0$ and hypothesis in, 2, about B_n' , it follows that

$$y_{n,2} \rightarrow 0 \text{ as } n \rightarrow \infty. \quad (4.6)$$

From the fact that B_n' increases monotonically to ∞ and $x_n \rightarrow 0$ it follows from Kroneker's theorem that

$$y_{n,1} \rightarrow 0 \text{ as } n \rightarrow \infty \quad (4.7)$$

thus (4.5), (4.6) and (4.7) establish (4.3) of \bar{B} .

(4.4) is covered by example 2 in (3.9); thus establishing \bar{B} .

5. *Proof of A.*—By the usual formula in Fourier series and Riemann-Lebesgue Lemma, we have

$$S_n(x_0) - f(x_0) = \frac{1}{2\pi} \int_0^\delta \{f(x_0 + t) + f(x_0 - t) \\ - 2f(x_0)\} \frac{\sin(n + \frac{1}{2})t}{\sin t/2} dt + \epsilon(n, \delta) \quad (5.1)$$

where $0 < \delta < \pi$, δ to be suitably chosen and fixed and $\epsilon(n, \delta) \rightarrow 0$ $n \rightarrow \infty$.

$$\text{Hence } \left| \frac{1}{B_n} \sum_{n_0}^n b_r S_{n-r}(x_0) - f(x_0) \right| \leq \frac{1}{2\pi B_n} \cdot \int_0^\delta \psi_{x_0}(t) \cdot \frac{|k_n(t)|}{\sin \frac{t}{2}} dt \\ + \epsilon'(n, \delta) \quad (5.2)$$

where $k_n(t) = \sum_0^n b_r \sin\left(n + \frac{1}{2} - r\right)t$ and

$$\epsilon'(n, \delta) = \left| \sum_0^n \frac{b_r \epsilon(n-r, \delta)}{B_n} \right| \rightarrow 0 \text{ as } n \rightarrow \infty.$$

We shall here prove

$$\left. \begin{aligned} (a) \quad \frac{|k_n(t)|}{\sin \frac{t}{2}} &\leq (2n+1) B_n \\ (b) \quad \frac{|k_n(t)|}{B_{\frac{1}{n}}} &\leq k_1 \text{ (some positive constant) in } \frac{1}{n} \leq t \leq \delta \end{aligned} \right\} \quad (5.3)$$

(a) follows from $\left| \frac{\sin mz}{\sin z} \right| \leq m$ for integral m .

Proof of 5.3 (b).

$$\begin{aligned} & - \sum_0^n b_r \sin\left(n + \frac{1}{2} - r\right)t \\ &= \text{Imaginary part of } \left\{ e^{-i\left(n+\frac{3}{2}\right)t} \cdot \sum_0^n b_r e^{i(r+1)t} \right\} \end{aligned}$$

$$\begin{aligned} \text{and } \sum_{r=0}^n b_r e^{i(r+1)t} &= \sum_{r=0}^{\left[\frac{1}{t}\right]} + \sum_{\left[\frac{1}{t}\right]+1}^n \left(\frac{1}{n}\right) \cdot \\ &= A_{n,1} + A_{n,2}. \end{aligned}$$

By hypothesis in 2 about b_n and Abel's inequality we have

$$|A_{n,2}| \leq \frac{k}{t} \cdot b_{\frac{1}{t}} \leq k' B_{1/t};$$

and

$$|A_{n,1}| \leq \cdot B_{1/t}.$$

Hence $|k_n(t)| \leq k_2 \cdot B_{1/t}$ in $\frac{1}{n} \leq t \leq \delta$ thus establishing (5.3) b.

$$\begin{aligned} \text{Now } \frac{1}{2\pi B_n} \int_0^\delta \psi_{x_0}(t) \frac{|k_n(t)|}{\sin \frac{t}{2}} dt &= \frac{1}{2\pi B_n} \int_0^{\frac{1}{n}} + \frac{1}{2\pi B_n} \int_{\frac{1}{n}}^\delta \\ &= E_n + F_n \end{aligned} \quad (5.4)$$

$$\text{By (5.3) a, } E_n \leq \frac{2n+1}{2\pi} \cdot \int_0^{\frac{1}{n}} \psi_{x_0}(t) dt.$$

and by Note 1, under B, hypothesis of \bar{A} or A, namely (3.1), implies

$$n \int_0^{\frac{1}{n}} \psi_{x_0}(t) dt \rightarrow 0 \text{ as } n \rightarrow \infty.$$

$$\text{Hence } E_n \rightarrow 0 \text{ as } n \rightarrow \infty \quad (5.5)$$

$$F_n \leq \frac{k_3}{2\pi B_n} \cdot \int_{\frac{1}{n}}^{\delta} \psi_{x_0}(t) \cdot \frac{B_{1/t}}{t} dt \text{ by 5.3 (b)}$$

$$\leq \frac{k_3}{2\pi B_n} \cdot \int_{\frac{1}{\delta}}^n \psi_{x_0}\left(\frac{1}{t}\right) \frac{B_t}{t} dt \text{ which by hypothesis of A}$$

$$\text{converges to 0 with } n \rightarrow \infty. \quad (5.6)$$

Hence (5.2), (5.5) and (5.6) establish \bar{A} (and with B, A also).

6. THEOREM C: If $f(x)$ be a periodic summable function and

$$(a) \frac{1}{B_x} \int_a^x \theta(t) \cdot b_t dt \rightarrow 0 \text{ or } (a') \frac{1}{x} \int_a^x \theta(t) dt \rightarrow 0 \text{ (a'')} \theta(x) \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$\text{where } \theta(t) = \psi_{x_0}\left(\frac{1}{t}\right) \cdot \frac{B_t}{t \cdot b_t}, \quad (6.1)$$

$$\text{and (b) the Fourier coefficients of } f(x) \leq \frac{A}{p_n}, (A > 0). \quad (6.2)$$

then the Fourier series of $f(x)$ converges at x_0 to $f(x_0)$;

the terms b_t , B_t , p_n , $\psi_{x_0}(t)$ being as follows:—

$$[(1) b_0 > 0;$$

$$(2) \frac{b_0}{b_1} \geq \frac{b_1}{b_2} \geq \dots \geq \frac{b_n}{b_{n+1}} \rightarrow 1 \text{ as } n \rightarrow \infty;$$

$$(3) \sum_0^n b_r = B_n \rightarrow \infty \text{ as } n \rightarrow \infty;$$

$$(4) b_t = b_{[t]}, B_t = B_{[t]};$$

$$(5) p_n \text{ is defined by } \frac{B_{[n^\delta]}}{B_n} \leq \delta < \frac{B_{[n^{1-\delta}]}}{B_n}, 0 < \delta < 1, (\delta \text{ being fixed});$$

$$(6) \psi_{x_0}(t) \text{ as in 1.1].} \quad (6.3)$$

Conditions (1), (2), (3) and (4) of (6.3) imply that b_n 's and B_n 's satisfy (1) and (2), (3) and (4) of 2,

Hence by theorems A and A₁, (6.1) implies that

$$\frac{1}{B_n} \sum_{r=0}^n b_r S_{n-r}(x_0) \rightarrow f(x_0) \text{ as } n \rightarrow \infty \quad (6.4)$$

In a paper⁸ to be shortly published, I have established the following Tauberian Theorem:—"Under conditions (1) to (5) about b_n , if a sequence S_n is such that

$$(a) \frac{1}{B_n} \sum_{r=0}^n b_r S_{n-r} \rightarrow S \text{ as } n \rightarrow \infty \text{ and } (b) S_n - S_{n-1} \leq \frac{A}{p_n} (A > 0)$$

then S_n converges to S in the ordinary sense. (6.5)

In view of this, conditions (6.2) and (6.4) establish theorem C.

7. *Special Cases of A and C.*—In these special cases we shall consider, the coefficients satisfy (6.3) thence the conditions of 2, so that we can consider the special cases of A and C, together.

(1) $b_n \sim \frac{1}{n^\sigma}$ $0 \leq \sigma < 1$. Theorem $\bar{A} \equiv$ (F. L. H.) theorem, and the Tauberian part of C = Cesaro-Tauber theorem for (C, r) $0 < r \leq 1$.

(2) $b_n = \frac{1}{n+1}$. Theorem A for this case is discussed in my paper⁷ Theorem C in this case is the Hardy-Littlewood⁵ (1932) test with slightly broader conditions.

(3) Corresponding to $b_n \sim \frac{1}{n \log n}$, $\frac{1}{n \log n \log \log n}$, etc., the point condition of A or A₁ gets stiffer and stiffer, and the Tauberian condition in C gets broader and broader, for example in the case $b_n \sim \frac{1}{n \log n}$, the point condition is in its simplest form is $\psi_{x_0}(t) \cdot \log t \cdot \log |\log t| \rightarrow 0$ $t \rightarrow 0$.

REFERENCES

- | | |
|-----------------------|--|
| 1. Zygmund | .. <i>Trigonometric Series</i> , 48-49. |
| 2. Fe Jer | .. <i>M.A.</i> , 1904, 58 , 501-69. |
| 3. Lebesgue | .. <i>Ibid.</i> , 1905, 61 , 251-80. |
| 4. Hardy | .. <i>P. L. M. S.</i> , 1913, 12 , 365-72. |
| 5. ——— and Littlewood | .. <i>J. L. M. S.</i> , 1932, 7 , 252-56. |
| 6. Valeron | .. <i>Rend di Palermo</i> , 1917, 42 , 267-84. |
| 7. K. S. K. Iyengar | .. "A Tauberian theorem and its application to convergence of Fourier series," this issue of <i>Proc. Ind. Acad. Sci.</i> , pp. 81-87. |
| 8. ——— | .. "Mercerian and Tauberian theorems for a class of Norlund means" (to appear shortly). |

THE BRIGHTNESS OF THE ZENITH SKY DURING TWILIGHT—PART II

BY DR. M. W. CHIPLONKAR

(S. P. College)

AND

J. D. RANADE

(Nowrosjee Wadia College, Poona)

Received July 6, 1943

(Communicated by Diwan Bahadur Dr. K. R. Ramanathan, D.Sc., F.A.Sc.)

Introduction

THE measurements of the brightness of the zenith sky during evening twilight at Colaba, Bombay, during the clear season of 1937–38 were discussed by one of the authors in a previous paper (referred to hereafter as Part I).¹ For a comparison of the brightness of the twilight sky with that calculated from Rayleigh's theory of molecular scattering of light, it is of importance to carry out exact photometric measurements under conditions of very clear skies. The observations at Bombay were affected to an unknown extent by scattered light from dust or other particles suspended in the atmosphere due to stray illumination from the city lights. † With a view to secure photometric measurements under conditions less affected by this, further experiments were carried out at two places: Poona (height above mean sea-level 1,830 ft.) and Mt. Sinhagad (height above mean sea-level 4,400 ft.). The present paper describes and discusses the results of these experiments carried out during the clear season of 1941–42.

Experimental

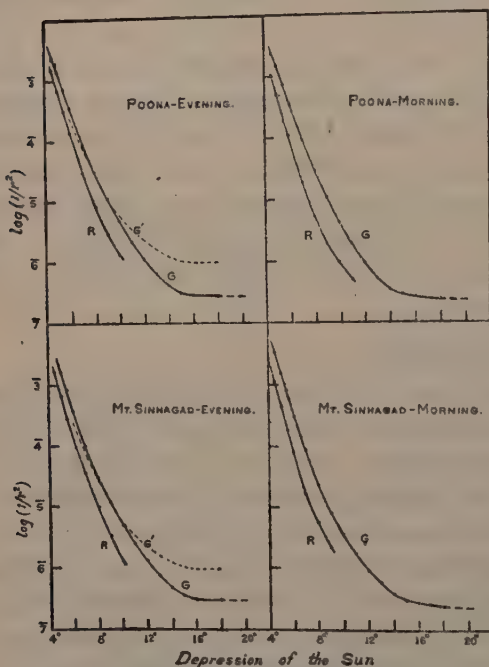
The photometric measurements were made with the same visual photometer described in Part I. The two sliding colour filters used in these experiments were: (1) Green, VG₁ (Schott and Genossen) and (2) Red, 27A (Wratten). Readings were taken for different positions of the sun below the horizon both before sunrise and after sunset during a large number of clear, moonless twilights. In these experiments the photometer lamp was fixed slightly nearer the magnesium oxide screen so that readings could be obtained for smaller depressions of the sun below the horizon (θ) than those obtained in Part I. Thus with the red filter, observations could be started when $\theta = 4^\circ$ and continued down to $\theta = 11^\circ$ while with the green filter they could be started when $\theta = 4^\circ 30'$ and continued down to $\theta = 18^\circ$ and even further. In taking measurements, one observer sat at the photometer in the dark room matching the brightness of the zenith sky with that of the Magnesium Oxide

screen at short intervals of time, while the other observer sitting outside the room noted down the corresponding readings of the ammeter and the chronometer and also from time to time the condition of the sky.

It must be mentioned here that the black-out restrictions during the period of observation at Poona proved to be of great advantage as they eliminated almost completely the stray illumination of the lowest layers of the atmosphere. Conditions at Mt. Sinhagad were still better since there was no question of stray illumination at all and the place is above the dust layer.

The calibration of the photometer lamp was carried out as described before in Part I, against the same standard Kodak Acetylene lamp using the two colour filters. The factor K , referred to before, required to convert ammeter readings to units of brightness in candles per square centimeter per unit solid angle, is equal to 0.090 for the green filter VG_1 (Schott and Genossen) and 0.128 for the red filter 27A (Wratten).

Results



The readings were grouped separately according to time, place and colour filter used. For every twilight, two curves, one for each filter, were drawn showing the variation of $\log(1/r^2)$ with the position (θ) of the sun below the horizon. The individual values in each group show little variation from the mean and therefore only an average curve was drawn for each group separately. Such average curves for Poona and Mt. Sinhagad are shown in Fig. 1. For the sake of comparison the Bombay evening curve for the green filter is also shown in the same figure.

Fig. 1. The brightness of the zenith sky as a function of the depression of the sun (in degrees) below the horizon

Brightness of zenith sky = $0.090/r^2$ for the green filter.

and " " = $0.128/r^2$ for the red filter.

To isolate the red region, Wratten red filter 27A and for the green region, Schott and Genossen green filter VG_1 were used. The broken curve represents observations made at Bombay with the same green filter.

The mean values of the intensities expressed in the above-mentioned units for different depressions of the sun below the horizon are given in Table I for each group separately. The numbers of observations from which the averages are obtained are given in brackets at the top of each column.

TABLE I

Logarithms of the brightness in candle power of the zenith sky at Poona and Mt. Sinhgad during twilight for different depressions of the sun below the horizon

Depression of the sun below the horizon	Poona				Mt. Sinhgad			
	Sunrise		Sunset		Sunrise		Sunset	
	Red <i>n</i> =(13)	Green (15)	Red (2)	Green (7)	Red (14)	Green (14)	Red (4)	Green (4)
4°	4.538
4° 30'	4.141	4.322	4.288	4.302	4.148	4.462	4.358	..
5°	5.805	4.132	5.928	4.082	5.748	4.127	5.938	4.172
5° 30'	5.378	5.822	5.608	5.812	5.383	5.802	5.588	5.882
6°	5.148	5.522	5.238	5.502	5.008	5.432	5.258	5.532
7°	6.378	6.922	6.578	6.892	6.338	6.892	6.658	6.952
8°	7.828	6.422	6.018	6.432	7.868	6.322	6.108	6.432
9°	7.388	7.982	7.558	6.002	7.428	7.862	7.638	6.032
10°	7.098	7.582	7.248	7.632	7.088	7.487	7.248	7.652
11°	8.798	7.242	..	7.292	8.728	7.182	..	7.352
12°	..	8.926	..	7.012	..	8.912	..	7.092
13°	..	8.672	..	8.762	..	8.742	..	8.852
14°	..	8.492	..	8.572	..	8.532	..	8.632
15°	..	8.402	..	8.442	..	8.432	..	8.522
16°	..	8.372	..	8.402	..	8.402	..	8.462
18°	..	8.322	..	(8.382)	..	8.332	..	8.452

Discussion

For the sake of comparison, average values of intensities for $\theta = 9^\circ$ to $\theta = 18^\circ$ obtained at different stations are brought together in Table II, after converting them into star magnitudes using the standard candle as an

intermediate step. It will be seen from this table that in general, smaller intensities were observed at Poona and Mt. Sinhadag than at Bombay. Considering the green filter curves at Bombay the initial rapid fall of intensity continues down to about $\theta = 10^\circ$ and then gradually reaches the final value of star magnitude 17.6 at about 15° – 16° . But at Mt. Sinhadag and Poona the initial rapid fall of intensity continues down to about $\theta = 14^\circ$ and then gradually attains the final value of about 19 star magnitude at $\theta = 16^\circ$ – 18° . The measurements made by Link² at Rysy show that for $\theta = 13^\circ$ the zenith sky there is brighter than that at Mt. Sinhadag and Poona for the same position of the sun below the horizon.

TABLE II

The average values of the intensities of the zenith sky expressed in star magnitude with respect to the standard candle, obtained at different stations for $\theta = 9^\circ$ to 18°

Depression of the sun below the horizon	Poona				Mt. Sinhadag				Bombay		Rysy.
	Sunrise		Sunset		Sunrise		Sunset		Sunset		
	Red	Green	Red	Green	Red	Green	Red	Green	Red	Green	Green
9°	16.53	15.50	16.11	14.99	16.93	15.35	15.91	14.92	16.30	14.95	14.15
10°	17.25	16.05	16.88	15.92	17.28	16.28	16.88	15.87	..	15.74	15.00
11°	18.01	16.89	..	16.77	18.18	17.05	..	16.62	..	16.27	15.85
12°	..	17.69	..	17.72	..	17.72	..	17.24	..	16.72	16.55
13°	..	18.32	..	18.09	..	18.15	..	17.87	..	17.11	17.20
16°	..	19.07	..	18.89	..	18.95	..	18.85	..	17.60	..
18°	..	19.19	..	19.05	..	19.17	..	18.87

There is also a marked difference between the morning and the evening curves, the evening twilight being on the average slightly brighter than the morning twilight. This is probably due to the greater scattering of light by the dust in the atmosphere during evening twilight than during morning twilight: during day dust is raised from the ground layers by convection currents. In the evening it begins to settle down and this process continues throughout the night. As small suspended particles scatter the incident light enormously in the forward direction, it may be expected that the twilight glow is stronger when there is a greater amount of dust present in the upper atmosphere. The effect of the dust in reducing the intensity of the scattered light on its vertical path downwards from the zenith sky can be shown to be of much less importance. Hence the zenith sky during evening twilight should be brighter than during morning twilight. The larger

values of intensities observed at Bombay for $\theta = 16^\circ - 18^\circ$ arises from a different cause and are to be attributed to the scattering of the light from the city lights. As pointed out before the measurements at Poona and especially those at Mt. Sinhadgad are less affected by this source of error.

The intensities observed at Poona and Mt. Sinhadgad for $\theta = 18^\circ$ (viz., 18.87–19.19 star magnitude) though distinctly smaller are comparable with the value of 18.76 star magnitude observed by Jean Dufay³ for the night sky during 1922–26, and with the mean value of 18.61* star magnitude observed by Bauer, Danjon and Langevin⁴, at Mont. Blanc for $\theta = 25^\circ - 29^\circ$. Thus, Jean Dufay's values are about 1.28 times, and those of Bauer, Danjon and Langevin about 1.49 times the values obtained by us. It appears that both these workers had not used any colour filters in their experiments while we used a green filter VG₁ (Schott and Genossen) which transmits only wavelengths between 4800 to 6000 Å.

To make a comparison of the absolute brightness of the night sky observed in India with those obtained in higher latitudes, it is proposed to continue these measurements of the twilight intensity further using the auroral filter.

Acknowledgements

The authors' best thanks are due to Dr. K. R. Ramánathan, Superintending Meteorologist, Meteorological Office, Poona, for his keen interest in this work and to the authorities of the Sir Parashurambhau College and Sir Nowrosjee Wadia College for providing the facilities to carry out this work.

REFERENCES

1. M. W. Chiplonkar .. *Proc. Ind. Acad. Sci., A*, 1941, **14**, 70.
2. F. Link .. The values are taken from the table in Gruner's article "Neueste Dämmerungsforschungen", in *Ergebnisse der Kosmischen Physik*, 1938, **Band 3**, 139.
3. Jean Dufay .. *Bulletin de l'observatoire de Lyons*, 1929, **Tome 11**, No. 2, 45–50.
4. Bauer, Danjon and Langevin *Comptes Rendus*, 1924, **178**, 2115. The values are quoted from Gruner's article referred to above.

* This value was given as 18.47 star magnitude in the former paper owing to a mistake in calculation.

A FURTHER STUDY OF ATMOSPHERICS DURING THE MONSOON PERIOD

BY DR. N. S. SUBBA RAO, M.A., PH.D.

(Annamalai University, Annamalai Nagar)

Received April 7, 1943

[Communicated by Prof. S. Ramachandra Rao, D.Sc. (Lond.), F.A.Sc.]

CONTENTS		PAGE
Introduction	127
Atmospherics during the period of transition	127
Atmospherics during the period of the winter monsoon	131
Discussion	135
Summary	138
References	139

Introduction

IN a previous paper I explained that atmospheric activity curves show certain distinctive features during the period of the S.W. (or summer) Monsoon. It was also shown that with the aid of these curves, the formation of a meteorological depression in the Bay of Bengal, its movement inland, and finally its weakening and disappearance could be followed. The curves further show that with the withdrawal of the monsoon, heat thunderstorms which occur mainly in the afternoons become more pronounced.

During the year 1941, the S.W. Monsoon withdrew from the country by about the end of September and the N.E. Monsoon later established itself. The present paper discusses with the aid of data collected in 1941, the characteristics of atmospheric activity of the period (1) between the withdrawal of the S.W. Monsoon and the setting in of the N.E. Monsoon and (2) during the period of the N.E. (or winter) Monsoon.

(1) *Atmospherics during the period of transition*

As typical instances of the atmospheric activity of this period, the atmospheric activity curves from the 1st to the 5th October 1941, will be considered in relation to the weather charts of the same period.

The atmospheric activity curves are given in Fig. 1. The peaks of activity in the figure may be divided into two groups, (i) peaks K, L and M of early morning activity and (ii) peaks A, B and C of atmospheric activity in the evening and early night. These two groups will be discussed separately.

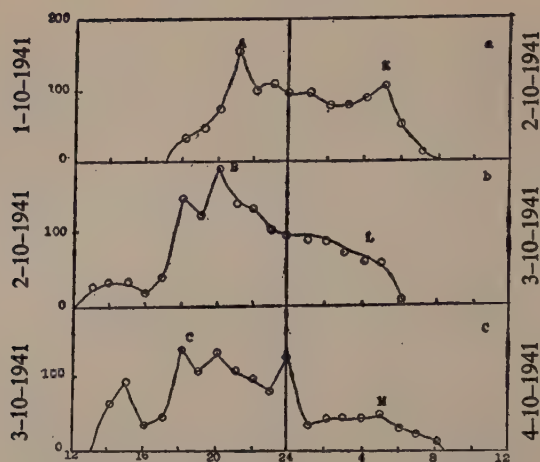
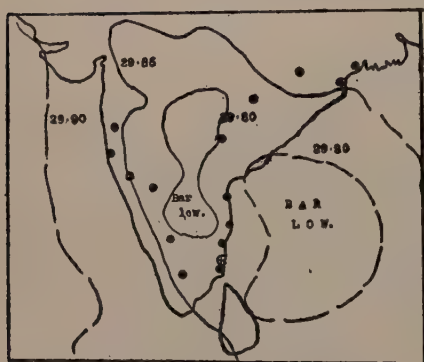
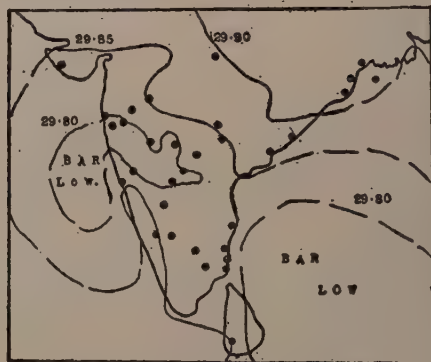


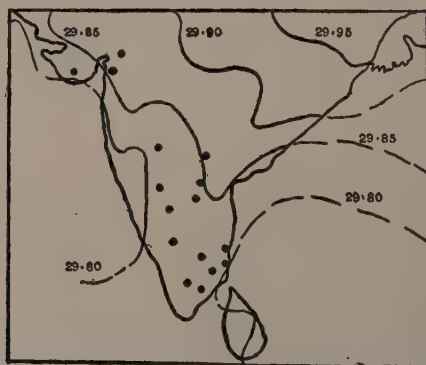
FIG. 1. Atmospheric Activity curves relating to the period of transition from the Summer to the Winter Monsoon



2 (a). 2-10-1941. At 8 hours.



2 (b). 3-10-1941. At 8 hours.



2 (c). 4-10-1941. At 8 hours.

Figs. 2a, 2b and 2c. Weather charts relating to the period of transition from the Summer to the Winter Monsoon

● Indicates places from which thunderstorms have been reported during the previous 24 hours.

⊕ Indicates the position of the University Laboratories at Annamalai Nagar.

Peaks K, L and M.—The weather charts relating to this period are given in Fig. 2. Figs. 2a, 2b and 2c show the distribution of isobars at 8 hours on the 2nd, 3rd and 4th October respectively. On the 2nd a depression appeared in the Bay of Bengal close to the coast. By the morning of the 3rd this region of low pressure became diffuse. By the 4th this became more diffuse and unimportant.

It was pointed out (1943) in a previous paper that the formation of low pressure regions on the sea is associated with observed atmospheric activity in the early mornings. The peak K on the morning of the 2nd may therefore be associated with the low pressure region in the Bay of Bengal in Fig. 2b. We notice further that as the low pressure region in the Bay of Bengal becomes more and more diffuse the atmospheric activity represented by L and M decreases. Thus the occurrence and variation of early morning activity represented by peaks K, L and M can without doubt be ascribed to the low pressure region in the Bay of Bengal.

Peaks A, B and C.—Taking next the atmospheric activity in the early night, it must be remembered that during the period of the summer monsoon, large peaks of activity appeared in the early night only when a depression which had formed in the Bay of Bengal crossed the coast and moved inland. The peaks A, B and C resemble peaks of activity which accompanied the movement inland of the depression. In the present case, however, as is evident from the weather reports in Fig. 2, the depression that formed in the Bay of Bengal on the 2nd remained practically in its original position and became unimportant by the 4th. The peaks of atmospheric activity A, B and C cannot therefore be attributed to the effect of this depression.

Fig. 2 further shows that during the period between the 1st and 4th October, a diffuse low pressure area moved across the peninsula from east to west. It was over the peninsula on the 2nd and was off the west coast of India on the 4th. This 'low' over the peninsula became regularly intensified in the afternoon as can be seen from an examination of the weather charts giving the distribution of isobars at 17 hours on these days. (The charts showing this distribution are not reproduced.) This intensification of the 'Low' over the peninsula in the afternoons which is a regular feature of the pressure distribution in the non-monsoon months brings about conditions favourable for thunderstorm activity and for the generation of atmospherics associated with such activity. The peaks A, B and C are the effects of this intensification of the low over the peninsula.

The differences in the appearances of the peaks A, B and C may be explained by a detailed study of the thunderstorm activity of the period.

The regions from which thunderstorm activity is reported in the daily weather reports on these days are indicated by black dots on the weather charts. These reports of the thunderstorm activity refer to the previous twenty-four hours and do not give any indication of the time of the day at which these thunderstorms were active. But a study of a large number of atmospheric activity curves along with the related reports of thunderstorms has shown that there is a greater probability of thunderstorm activity along the coast line, occurring in the later part of the night, specially when a low pressure region exists on the sea and close to the coast. It would in this connection be extremely useful to analyse the actual times of occurrence of thunderstorms. This could not however be carried out for want of necessary data.

It was pointed out in an earlier paper (1943) that if thunderstorms are reported from a large number of areas, it is very unlikely that all these centres are active at the same time. The activity at one centre may be on the decline while that at another is reaching a maximum. Thus data on atmospherics collected from one observing station which cannot distinguish between atmospherics coming from various centres, is likely to show certain characteristic features. If only one narrow region is affected there will be a definite rate of increase of atmospheric activity, which will reach a maximum terminating in a peak, and after which there will be a regular decline resulting finally in zero activity. The atmospheric activity curve may therefore be expected to give a sharp well-defined peak of activity, the rise and decline of activity being very steep. If during a certain period, a large number of centres are active, assuming that the maximum activities at every centre do not necessarily coincide in time, the atmospheric activity curves will show large activity for a considerable time and well-defined peaks are not likely to be observed.

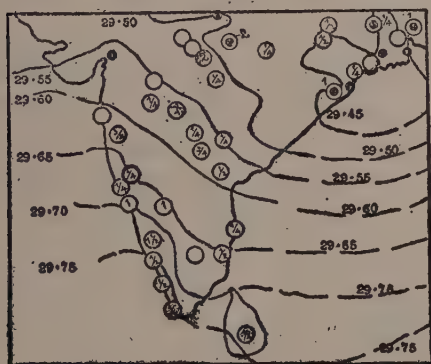
The low pressure areas on the evenings of the 1st and 2nd are concentrated into a narrow region while that on the 3rd is over a very large region. The areas from which thunderstorm activity is reported lie on the outskirts of the region of low pressure. It is no wonder therefore, that atmospheric activity in the evenings and early night shows sharp peaks like A and B as on the 1st and 2nd, while on the 3rd atmospheric activity at a large value continued from 18 to 24 hours and there are three peaks instead of one.

Thus during the period of transition large peaks of activity are observed in the evenings and the early night. This activity is governed mainly by the low pressure regions which develop in the centre of the peninsula and intensify by the evening each day during this period. Atmospheric activity in the later part of the night is on a small scale.

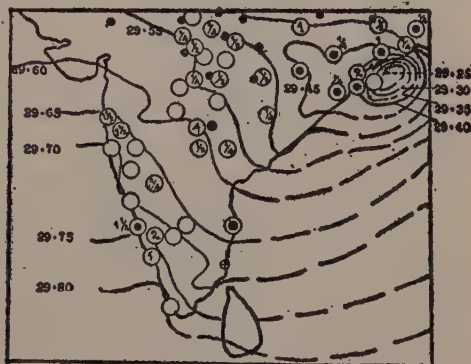
(2) *Atmospherics during the period of the Winter Monsoon*

Several observers have noticed that atmospheric activity during the winter months is on a much smaller scale than in the warmer months. One of the earliest of these is Jackson (1902) who noticed that Atmospherics are more frequent in summer and autumn than in winter and spring. Later, Wolf (1922) found that while during the warm half year atmospherics developed on the appearance of a new depression and disappeared on its filling up, no such relation could be noticed in winter. He says that even thunderstorms failed to give a notable increase in Atmospheric disturbance in winter. Watt (*Nature*, Vol. 127) found that the predominant source of the world's supply of Atmospherics lies in a region of summer afternoon.

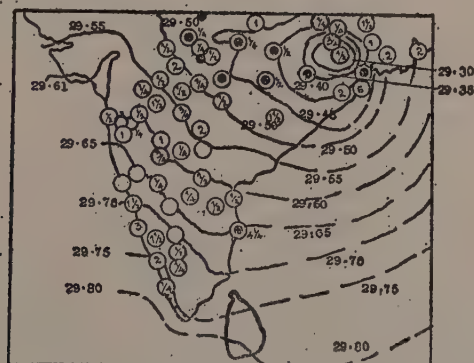
These statements are based on observations in temperate climates. The present paper deals with observations recorded at Annamalainagar, from



3 (a). 7-8-1941. At 8 hours.



3 (b). 8-8-1941. At 8 hours.



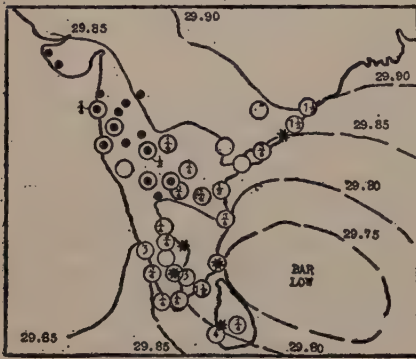
3 (c). 9-8-1941. At 8 hours.

FIGS. 3a, 3b and 3c. Weather charts relating to the period 7th to 10th August 1941 during the Summer Monsoon

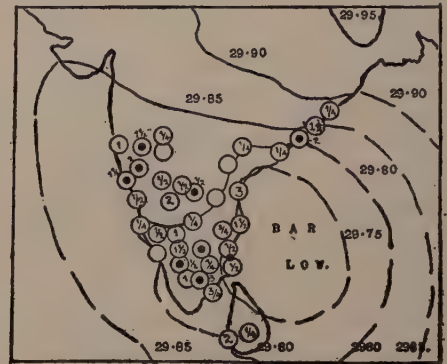
- Indicates places from which rainfall is reported, the amount of rainfall during the previous 24 hours being indicated by the numbers inside the circles.
- Indicates places from which thunderstorms during the previous 24 hours have been reported.

October to December 1941 during the period of the winter monsoon. A study of atmospheric activity during this period shows no regular features of the type found in the period of the summer monsoon, and described by me in an earlier paper. I propose to discuss in this paper the probable causes for the striking difference noticed in the behaviour of Atmospherics during the two periods.

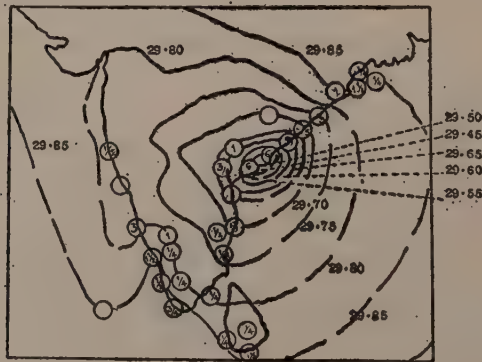
Two sets of weather charts, taken from the Indian Daily Weather Reports, are redrawn in Figs. 3 and 4. The first set refers to the period 7th–10th



4 (a). 5-10-1941. At 8 hours.



4 (b). 6-10-1941. At 8 hours.



4 (c). 7-10-1941. At 8 hours.

FIGS. 4a, 4b and 4c. The weather charts relating to the period 3rd to 8th October 1941 during the Winter Monsoon

- Indicates places from which rainfall is reported, the amount of rainfall during the previous 24 hours being indicated by numbers inside the circles.
- Indicates places from which thunderstorms during the previous 24 hours have been reported.
- * Indicates areas where thunderstorm activity attributable to the depression in the Bay of Bengal has occurred.

August 1941, during the summer monsoon and the other to the period 3rd–8th October 1941, the beginning of the North East Monsoon.

On these charts the circles indicate the regions from which rainfall is reported, during the previous 24 hours, the actual amount of rainfall being indicated by the numbers inside the circles. According to the convention followed in the mapping out of these charts rain less than $\cdot 09''$ is neglected. A blank circle indicates rainfall between $\cdot 10'' - \cdot 17''$.

$\frac{1}{4}$	—	$\cdot 18''$ to $\cdot 37''$;
$\frac{1}{2}$	—	$\cdot 38''$ to $\cdot 87''$;
$\frac{3}{4}$	—	$\cdot 68''$ to $\cdot 87''$;
1	—	$\cdot 88''$ to $1\cdot 24''$;
$1\frac{1}{2}$	—	$1\cdot 25''$ to $1\cdot 74''$;
2	—	$1\cdot 75''$ to $2\cdot 50''$;
3	—	$2\cdot 51''$ to $3\cdot 49''$, etc.

Weather charts in Figs. 3 and 4.—The charts refer to two similar cyclonic storms, one during the S.W. Monsoon and the other during the N.E. Monsoon. In their wake they brought considerable rain to the regions affected, *viz.*, Bengal and Orissa in the first case and S.E. Madras in the second case. In this respect therefore the two cyclonic storms are very similar.

Thunderstorm activity during these periods.—If we compare the thunderstorm activities during these periods we find a striking contrast. Areas from which thunderstorms are reported during the previous 24 hours are indicated by black dots in the weather charts. It is evident from Figs. 3a and 3b, that the deepening of the depression into a cyclonic storm is followed by increased thunderstorm activity. Thunderstorms are reported from a large number of areas and their positions give an indication of the probable direction of travel of the cyclone. In Fig. 3c, we find that as the depression slowly fills up thunderstorm activity is again on the decrease.

It will be clear from the above that thunderstorm activity increases with the deepening of the depression. The position of the areas of thunderstorm activity is mainly governed by the region of low pressure and the activity becomes feeble as the low pressure region fills up.

In Fig. 4a, we notice thunderstorm activity at certain places in the Peninsula, a large number of areas to the N.W., a few in the south of the Peninsula and a few along the east coast. From Fig. 4b, we find that the depression moved nearer the coast line. In striking contrast to what was noticed in the set of charts given in Fig. 3, we find that with the approach of the depression towards land thunderstorm activity is reported from fewer areas and is hence on the decline. In Fig. 4c, we find that the intensification of the depression into a cyclonic storm close to the coast between Masulipatam

and Cocanada caused widespread heavy rain along the Madras coast and the adjoining districts but no thunderstorms occurred in any of these areas.

Thus we find that thunderstorm activity which increases during the summer monsoon with the intensification of a depression, disappears under similar conditions during the winter monsoon. As most atmospheric orginate in areas of thunderstorm activity, it is no wonder that atmospheric activity during the period of the summer monsoon shows certain regularities, increasing activity being associated with the formation and accentuation of a depression and its decreasing activity with the movement and disappearance of the low pressure region. In the period of the winter monsoon these features are not noticed.

In this connection one other point may also be mentioned. In Fig. 4a the presence of a large number of thunderstorm areas might create an impression that thunderstorm activity is very much greater and further that all these might be due to the effect of the depression formed in the Bay of Bengal. A study of the weather charts for the previous two days, *i.e.*, 3rd and 4th, helps us to determine the true effect of the depression in the Bay of Bengal.

On the 2nd October a depression in the Bay was accompanied by a region of low pressure in the central region of the Peninsula. The chart for this day is given as Fig. 2b and thunderstorms were reported from areas lying on the coast line on either side of the land depression.

Judging from the way in which the areas of thunderstorm activity appear and disappear during the three days, 2nd, 3rd and 4th October, it appears as though the activity in the N.W. region of the Peninsula may be attributed to the depression on land noticed on the 4th and to the depression in the Arabian Sea (Fig. 2c). We are thus left with a few areas only, areas which showed no variation with the appearance or disappearance of the depression in the Arabian sea, or the depression on land. These areas are indicated in the figure thus✱. It will thus be evident that even when thunderstorm activity is reported and atmospheric are recorded at the observing station, they arise only from small isolated areas and that the total atmospheric activity itself is small.

One example may be given to show how small the atmospheric activity is when it exists. A deep depression formed in the Bay of Bengal on the 30th of November intensified into a cyclonic deprcssion on the 1st December, became severe and passed inland by the night of the 2nd. Later this moved right across the Peninsula and entered into the Arabian Sea by the 4th and became unimportant by the 6th.

This particular example is of special interest as the cyclonic storm passed almost over the observing station. If there had been atmospheric activity of the intensity usually met with in the summer monsoon period, no record could have been obtained, as the recording equipment would have been upset on account of the powerful impulses given to the galvanometer. Although a few atmospherics were actually recorded during this period, the atmospheric activity must be judged as being of negligible amount, the little activity that was observed being attributable to very feeble isolated lightning flashes possibly occurring far above the monsoon clouds, invisible from the ground and unaccompanied by thunder. As the convention in the Indian Meteorological Department is that thunderstorm should be reported only when thunder is heard with or without precipitation, the Weather Reports do not mention any thunderstorm during this period.

Discussion

As stated already during the period of the Summer monsoon thunderstorm activity and the associated Atmospheric activity are on a large scale, while during the Winter monsoon they are of negligible amount. It was also pointed out that atmospheric activity is intimately connected with meteorological depressions, and that the study of the variation of Atmospheric activity from hour to hour and day to day enables us to follow the various stages in the formation, accentuation, movement inland and the subsequent filling up of the meteorological depressions that originate in the Bay of Bengal during this period.

It may be considered surprising that there is only a small amount of thunderstorm and Atmospheric activity during the period of the winter monsoon. Further, as has been already pointed out, the little Atmospheric activity that does exist, becomes feeble on the intensification of a depression.

Brunt (1934) considers the greater frequency and intensity of the meteorological depressions in Europe in winter as due to the larger differences of temperature between the pole and the equator in winter than in summer. The reason for the feeble thunderstorm activity during this period may be understood from a discussion of the various features involved in the formation of depressions and the generation of thunderstorm and the associated Atmospheric activity.

The most important of these factors is Solar Radiation. The effect of the sun in bringing about conditions favourable for the display of energy automatically in the atmosphere in the form of a thunderstorm is described by Napier Shaw and Captain Douglas. According to Napier Shaw (1930) the first condition to be satisfied is the existence of a state of liability in the atmosphere

caused by the establishment of a thick layer in convective equilibrium. Another condition is the provision at the right moment, of a sufficient quantity of air saturated with water vapour. Both these conditions are governed by the effect of Solar Radiation.

Convection on a large scale in air of a high degree of humidity is essential for the production of towering cumulus clouds whose base, according to Captain Douglas (1923) is usually between 5,000 to 6,000 feet, in severe thunderstorms, and whose tops attain 20,000 feet in summer and 15,000 feet in winter. Captain Douglas also states that the existence of at least one damp layer as low as 6,000 feet appears to be a necessary condition for the development of thunderstorms.

The electrification of thunderclouds is explained by the well-known theories of Wilson and Simpson. The mechanism suggested by Wilson as the cause of opposite charges on large and small drops inside a thundercloud depends upon the presence in the cloud of a number of slow ions. In the earlier stages of development of a thundercloud these may arise from natural sources, but later on they will be supplied in numerous numbers by brush discharges from water drops (Macky, 1933) drawn out by the field into pointed forms (Schonland, 1932). According to Simpson (1927) the generation of electricity is a consequence of the disruption of rain drops when caught in a vigorous convection current. A water drop with a radius of more than 0.25 cm. becomes flattened out and unstable when it falls through the air with the result that it breaks up into a number of smaller drops. Since the terminal velocity of a falling drop with a radius of 0.25 cm. is 8 metres per second, it follows that no drop of water can ever fall downward through an ascending current of air whose vertical velocity exceeds 8 metres per second.

Formation of a meteorological depression.—Convection again plays an important part in the formation of depressions. The formation of a depression involves the removal of large amounts of air for the fall of pressure. All theories put forward for explaining the formation of a depression are based on the existence of horizontal differences of temperature and the displacement of warm air by cold air. According to Brunt (1934) the most obvious method of removal of air is by means of a convection current, produced by inequalities of temperature, or water vapour content or by the effect of surface discontinuity. If warm damp air is set in motion by its buoyancy the continuance of the upward motion as an effect of the condensation of moisture is easily understood. Such an ascending current has a scouring effect on the environment, the process being aptly described as 'eviction of air'.

It is thus seen from the above that vigorous convection plays a most important role in the formation of cumulus clouds, in the generation of electrical charges in thunderclouds and also in the formation of depressions. Convection is dependent on Solar Radiation and therefore it would be instructive to consider how these effects are modified by the varying amounts of solar radiation received at various parts of the globe and at the various seasons.

It is well known that thunderstorms are more frequent and more violent in the tropics. Simpson (1927) attributes this in the first place, to the larger water vapour content of the air in the tropics which provides the greater energy for driving the currents upwards to much greater heights. Secondly, the height at which the freezing point is reached is much greater and finally the stratosphere is so much higher that there is more vertical room in which the thunderstorms can develop. By an extension of the same argument, the cause of the smaller thunderstorm activity during the period of the winter monsoon as compared with that of the summer monsoon may be traced to the lower temperatures during the former period.

There seems to be no doubt that convection is quite vigorous during the period of the winter monsoon. Napier Shaw (1930) points out that rainfall is the best index of convection and that the absence of rainfall is equally good evidence of the absence of any persistent ascending current. The large amount of rainfall that occurs on the outskirts of the depressions formed during the period of the monsoon, in the Bay of Bengal, is sufficient evidence of the existence of convection on a large scale. But there is no thunderstorm activity in spite of the large convection.

Brunt (1934) points out that in addition to the mechanism that gives rise to vertical convection in any region where a lowering of pressure is taking place, there must be present some mechanism for removing the air that has ascended. Otherwise this vertical motion cannot continue for any length of time. The simplest mechanism that may be thought of is an upper current whose direction differs from that of the current in the lower troposphere. Brunt takes the outward motion of cirrus clouds from the centre of a cyclonic system as evidence of the existence of such a current. In the absence of some means of removal of the evicted air a thunderstorm is a more likely occurrence than a cyclonic system. The absence of thunderstorm activity during the winter monsoon period even when vigorous convection is taking place may probably be due to the causes enumerated above.

Finally there is also the conductivity of the atmosphere. Considering the smaller space, in which thunderstorms during the winter may develop,

the intensity of the depressions formed during the period and the large amount of rainfall accompanying the formation of cyclonic systems, it may be expected that the conductivity of the atmosphere may rise to large amounts and give rise to leakage effects. Schonland (1932) from a study of the recovery curves of a thundercloud after a discharge showed that the electrical energy generated by the storm is only partially employed in the feeding of the flashes. At the moment just before the discharge most of the power of the machine is expended in overcoming various leakage effects. If the conductivity of the atmosphere becomes very large, it may happen that the potential of the thunderclouds may never reach the sparking value.

A review of recent work on Atmospherics in Nature (1936) states that it is now generally agreed that the majority of atmospherics encountered in Radio Communication originate in lightning flashes. When the storm is close to the receiver it is possible to identify the stronger atmospherics with the neighbouring flashes. It is therefore quite easy to understand that if the potential of the thunderclouds does not attain the sparking value no lightning flashes can occur and hence the amount of Atmospheric activity must be very small indeed.

Some observations on the variation of Atmospheric activity with precipitation and conductivity lend support to the above view. Wiedenhoff (1921) found that atmospheric activity was at a minimum with maximum conductivity at a moderate height with overcast sky, with maximum relative humidity and minimum temperature. Rothe (1921) found that atmospherics produced by storm clouds cease as soon as uniform rain starts.

Thus the striking difference in the variation of Atmospheric activity in the periods of the Summer and the Winter Monsoon may be traced to (i) the lower temperature, (ii) the smaller height available for the development of thunderstorm activity, (iii) the operation of a mechanism by which the ascending current of air is removed by means of an upper air current and (iv) the larger leakage effects that are likely to prevent the charges in the cloud building up to the sparking value.

Summary

The paper discusses the characteristics of Atmospheric Activity during (i) the period of transition from the South West (or the summer) monsoon to the North East (or the Winter) monsoon, and (ii) the North East (or the Winter) monsoon.

During the period of transition large peaks of activity are observed in the evenings and the early night. This activity appears to be governed mainly by the pressure regions which develop in the centre of the Peninsula by

the evening each day during this period. Activity in the later part of the night is on a small scale.

It was pointed out in a previous paper that during the summer monsoon, unsettled conditions in the Bay of Bengal give rise to continuous Atmospheric Activity throughout the night; the formation of a depression is accompanied by large atmospheric activity in the early mornings; the movement of the depression inland by an increase in early night activity and the disappearance of early morning activity. It was further shown that the various stages in the formation, movement inland and finally the filling up of the depression could be followed with the aid of the Atmospheric Activity curves.

During the period of the North East Monsoon, however, there is a striking contrast. With the setting in of the monsoon the atmospheric activity becomes very feeble. Further, the little activity that does occasionally exist disappears on the accentuation of depressions that are formed in the Bay of Bengal and the Arabian Sea during this period.

In the later part of the paper the probable causes for this difference in behaviour are discussed. It is suggested that this difference in behaviour may be due to (i) the lower temperatures, (ii) the smaller height available for the development of thunderstorm activity, (iii) the operation of a mechanism by which the ascending current of air is removed by an upper air current, and (iv) the larger leakage effects that are likely to prevent the charges in the cloud from building up to the sparking value.

In conclusion I have much pleasure in expressing my thanks to Dr. S. Ramachandra Rao, D.Sc. (London), Professor of Physics, for valuable guidance and helpful criticism.

REFERENCES

- | | | |
|--------------------|----|---|
| Brunt | .. | <i>Physical and Dynamical Meteorology</i> , Camb. Univ. Press, 1934. |
| Douglas, Captain.. | | <i>Dictionary of Applied Physics</i> , 1923, 111 , 41. |
| Jackson | .. | <i>Proc. Roy. Soc.</i> , 1902, A 70 , 266. |
| Mackay | .. | <i>Ibid.</i> , 1933, A 133 , 565. |
| Marchand | .. | <i>Rev. Gen. Sc.</i> , Paris, 1921, 32 , 594. |
| Rothe | .. | <i>C. R. Acad. Sc.</i> , Paris, 1921, 175 , 840. |
| Schonland | .. | <i>Atmospheric Electricity</i> , Methuen's Monographs on Physical subjects, 1932. |
| Shaw, Napier | .. | <i>Manual of Meteorology</i> , Camb. Univ. Press, 1930, 111 , 280. |
| Simpson | .. | <i>Proc. Roy. Soc.</i> , 1927, A 114 , 376. |
| Subba Rao | .. | <i>Proc. Ind. Acad. Sci.</i> , 1943, 17 , 83. |
| Watt, Watson | .. | <i>Nature</i> , 1925, 127. |
| Wiedenhoff | .. | <i>Jahrb Draht Telegraph</i> , Berlin, 1921, 18 , 242. |

A STUDY OF 'CARPASEMINE' ISOLATED FROM CARICA PAPAYA SEEDS

BY T. B. PANSE AND A. S. PARANJPE

(Pharmacology Department, Seth G. S. Medical College, Parel, Bombay)

Received July 21, 1943

(Communicated by Dr. K. Venkataraman, F.A.Sc.)

THE seeds of *Carica papaya* are said to possess powerful anthelmintic and emmenagogue properties.¹ In order to verify these claims and other medicinal properties claimed for the seeds, a pharmacological study of the seeds was undertaken and as a part of the work the chemical analysis of seeds was first carried out.

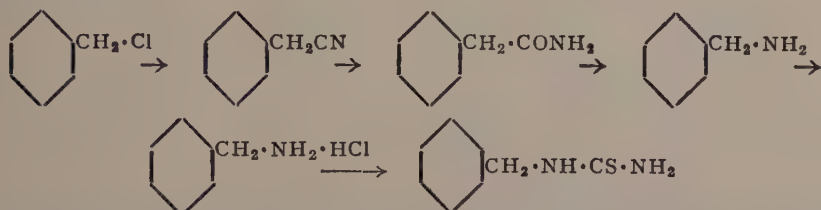
Reference to previous work on the subject showed that Greshoff² had isolated mainly from the leaves (and is also stated to have obtained from the fruit and seeds) of *Carica papaya* Linn., the alkaloid Carpaine, m.p. 121°. We have, however, isolated from the seeds a crystalline substance, melting at 165°. In a preliminary note³ on the substance it was provisionally named 'Carpasemine' because of its alkaloidal character, such as the presence of nitrogen in the molecule and positive results for tests with reagents for alkaloids.

A careful examination of the constituent elements in the substance showed that it contained sulphur (instead of O₂ as was assumed in our previous note) together with carbon, hydrogen and nitrogen. The results of the ultimate analysis of the substance as well as those of its molecular weight determination by cryoscopic method, indicated the molecular formula to be C₈H₁₀N₂S, for the substance. The substance gave an acetyl derivative, m.p. 131° and also formed a methiodide compound, m.p. 103°. However, it did not form salts with the common acids. On boiling the substance, m.p. 165°, with sodium hydroxide, an "oil" (A) and a product (B), m.p. 148-9° (in low yield), were obtained. Evolution of ammonia was noticed during the reaction. The "oil" (A) formed a hydrochloride, m.p. 245-6°. While the product (B) formed an acetyl derivative, m.p. 130° and was not found to contain sulphur. On oxidation, the product (B) yielded a compound, m.p. 205-7°, which is under investigation. During the oxidation a distinct smell of benzaldehyde was noticed. Direct oxidation of the original substance, m.p. 165°, however yielded benzoic acid.

The oxidation results indicated that the substance, m.p. 165°, contained a benzene ring with a side chain. Evolution of ammonia on boiling with sodium hydroxide, suggested it to be a substituted ammonia derivative, which could also form acetyl and methiodide compounds. While its weak

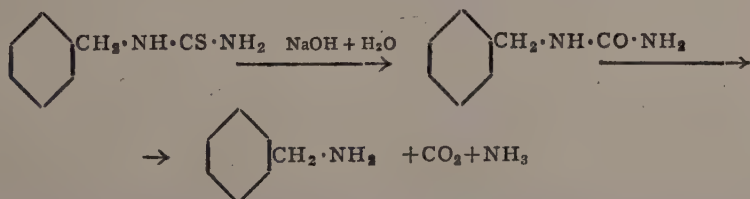
basic character together with the fact that it contained sulphur indicated it to be a phenyl derivative having probably as its side chain a heterocyclic ring containing S and N or a thiourea residue.

On referring to the literature, it was found that benzylthiourea (or benzylthiocarbamide) possessed properties similar to those enumerated for the substance, m.p. 165°. In order to confirm this assumption, a direct comparison of the natural product and synthetic benzylthiourea was considered necessary. The synthetic benzylthiourea was prepared by the scheme indicated below :—



The mixed melting point of the product, m.p. 165° isolated from the papaya seeds with the synthetic benzylthiourea (Salkowski)⁴ showed no depression and thus established the identity of the former with the latter. The identity was further confirmed by the mixed melting point of their acetyl derivatives.

It is known that substituted thioureas when boiled with aqueous alkali decompose into a substituted amine, carbon dioxide, hydrogen-sulphide and ammonia. In view of this fact, the "oil" (A) obtained on boiling the substance, m.p. 165° with alkali, was suspected to be benzylamine. The surmise proved to be correct as the mixed melting point determination of the hydrochloride of (A) and the hydrochloride of benzylamine showed no lowering. The other product (B) obtained on boiling the substance m.p. 165° with alkali, appeared from its properties to be benzylurea (or benzylcarbamide). It was subsequently identified to be benzylurea by a mixed melting point with synthetic benzylurea (Paterno and Spica).⁵ The action of 20% aqueous sodium hydroxide solution on benzylthiourea may, on the basis of the results obtained above, be represented as follows :—



The course of the reaction also explains the low yield of the intermediate product, benzylurea, in view of the possibility of its further hydrolysis into benzylamine, carbon dioxide and ammonia.

The pharmacological study of benzylthiourea or 'carpasemine' is in progress and the results of the investigation will be published elsewhere in due course.

Experimental

Isolation of the substance, m.p. 165°, from Carica papaya Seeds.—Dried papaya seed powder (100 gm.) was digested in Prollius's fluid (approx. 550 c.c.) with occasional shaking during forty-eight hours. The liquor was then filtered off and the seed powder discarded. The filtrate was allowed to evaporate at the room temperature, when an oil together with some solid was obtained as a residue. The solid after separation from the oil was crystallised from boiling water. The repeated crystallisations of the solid resulted in the formation of beautiful bunches of colourless crystals, m.p. 165°, yield 0.35% of the seed powder. It may be mentioned here, that the yield of the substance was seriously hampered when the seeds were powdered long before the extraction. Analysis (Found: C, 57.95, H, 6.44, N, 16.3, S 19.3%, $C_8H_{10}N_2S$ requires C, 57.8, H, 6.0, N, 16.9, S, 19.3%). The molecular weight of the substance (determined by the cryoscopic method, using nitrobenzene as solvent) was found to be 163 which indicated the molecular formula $C_8H_{10}N_2S$ for the substance. The substance is bitter to taste. It is insoluble in cold water, petroleum ether and benzene but fairly soluble in alcohol and acetone. A mixed melting point of the substance with benzylthiourea (Salkowski,⁴ m.p. 164°) showed no depression.

Acetyl derivative of the product, m.p. 165°—was prepared with sodium acetate and acetic anhydride as usual. The acetate crystallised from 40% alcohol into prisms, m.p. 131°. Analysis (Found: N, 13.2%; $C_{10}H_{12}N_2OS$ requires N, 13.46%). The mixed melting point of this acetate with the acetate of benzylthiourea (Werner,⁶ m.p. 129–30°) showed no depression.

Methiodide of the product, m.p. 165°.—Equimolecular quantities of methyl iodide and the product, m.p. 165°, were added to methyl alcohol and refluxed on a water-bath for four hours. Alcohol was then distilled off and a sticky residue was obtained. The residue, which solidified on keeping, was crystallised from benzene into fine hexagonal crystals, m.p. 103–5°. Analysis (Found: N, 9.1%, $C_9H_{13}N_2SI$ requires N, 9.0%). The product was fairly soluble in water.

Oxidation of the product, m.p. 165°.—0.5 Gm. of the product, m.p. 165°, was dissolved in warm water and (30 c.c) of potassium permanganate solution (2%) was added to it in dropwise manner. After the reaction was over the manganese dioxide precipitate was filtered off. The excess of potassium permanganate in the filtrate was then destroyed with a few drops of alcohol and manganese dioxide precipitate again filtered. The resulting clear filtrate,

on cooling was extracted with ether, which on dehydration with anhydrous sodium sulphate followed by evaporation yielded a solid, m.p. 120°. It was identified as benzoic acid.

The action of alkali on the product, m.p. 165°.—0.5 Gm. of the product, m.p. 165°, was refluxed with 20% aqueous sodium hydroxide solution (75 c.c.) for four hours. During the reaction a distinct smell of ammonia was perceptible. The alkaline reaction mixture on cooling, was extracted with ether. Dehydration of the ethereal layer with anhydrous calcium chloride followed by evaporation gave a crystalline solid and an oil. The solid was separated from the oil and crystallised from benzene into light lustrous needles, m.p. 148–9°. Yield 7%. Analysis (Found: C, 64.52; H, 6.75; N, 18.57%; $C_8H_{10}N_2O$ requires C, 64.00, H, 6.4, N, 18.66%). A mixed melting point of the product, m.p. 148–9°, with benzylcarbamide (Paterno and Spica,⁵ m.p. 147°) prepared from benzylamine and potassium cyanate showed no depression.

Acetate of the product, m.p. 148–9°—was prepared with sodium acetate and acetic anhydride as usual. The acetate was crystallised from boiling water and was found to melt at 130°. Analysis (Found: C, 62.95, H, 6.42, N, 14.55%; $C_{10}H_{12}O_2N_2$ requires C, 63.0, H, 6.25, N, 14.6%).

Oxidation of the product, m.p. 148–9°.—0.225 Gm. of the product m.p. 148–9°, was dissolved in warm water and 15 c.c. of potassium permanganate solution (2%) was added to it in a dropwise manner. During oxidation bitter almond-oil-like smell was noted. After the reaction was complete, the manganese dioxide precipitate was filtered off. The excess of potassium permanganate in the filtrate was destroyed with a few drops of alcohol and the precipitate of the manganese dioxide again filtered off. The resulting clear filtrate was concentrated on a water bath and on cooling, deposited beautiful hexagonal crystals, m.p. 205–7°. The product is under further investigation.

Hydrochloride of the oil obtained in the alkali boiling of the product, m.p. 165°.—A few drops of the oil were treated with conc. hydrochloric acid when a solid was thrown down immediately. The solid crystallised from alcohol into thin rectangular plates melting at 245–6°. The hydrochloride did not show any lowering in the melting point when admixed with benzylamine hydrochloride (Curtius and Lederer,⁷ m.p. 246°).

Synthesis of Benzylthiourea.—To a warm solution of sodium cyanide (52 gms.) in water (45 c.c.) was slowly added benzyl chloride (103 gm.) diluted with equal volume of alcohol. The reaction was completed by heating on a water-bath for three hours. Sodium chloride was removed by filtration and alcohol distilled off from the filtrate. Benzyl cyanide separated as an oil from the residual aqueous portion and purified by distillation under reduced pressure 10 mm. had a b.p. 115–20°. (Cannizzaro,⁸ b.p. 115–20°.) Yield

80 gm. benzyl cyanide (10 gm.) prepared as above was mixed and shaken with sulphuric acid (15 gms. D. 1.82) care being taken that the temperature is not raised above 65–70°. After the heat of the reaction was over, the mass was poured in water. The resulting precipitate of phenylacetamide was purified by treatment with sodium bicarbonate solution, followed by washing with water and crystallisation from hot water, m.p. 155° (Purgotti,⁹ m.p. 155–6°). To 135 gm. of phenyl acetamide (1/10 mol.) prepared as above was added bromine (8.0 gm. 1/10 mol.) dissolved in 4 molecular proportions of potassium hydroxide in 16 parts of water. The solution was heated rapidly and as soon as a clear solution was formed, it was distilled off to obtain benzylamine as an oil in the distillate, b.p. 185° (Hoogewerff and van Dorp,¹⁰ b.p. 185°). The benzylamine by treatment with hydrochloric acid was converted into its hydrochloride, m.p. 245° (Curtius,⁷ m.p. 246°). The hydrochloride on heating with equimolecular quantity of potassium sulphocyanide at a temperature of 120° for fourteen hours, yielded a brownish residue which after washing with cold water, was crystallised from boiling water into colourless needles. The benzylthiourea melted at 164° (Salkowski,⁴ m.p. 164°). Yield 80%.

Summary

From the seeds of *Carica papaya* a substance, m.p. 165° ($C_8H_{10}N_2S$) has been isolated for the first time and named 'Carpasemine' to indicate its source. The chemical properties of 'Carpasemine' together with its degradation products have been studied and some new derivatives have been prepared from it. 'Carpasemine' has been identified to be benzylthiourea or benzylthiocarbamide by mixed melting point with the synthetically prepared benzylthiourea. The identity has also been confirmed through the mixed melting point of their derivatives.

The present investigation forms a part of the Indigenous Drugs Inquiry financed by the Indian Research Fund Association, to which our thanks are due.

REFERENCES

- | | |
|-----------------------------|--|
| 1. Kirtikar and Basu | .. <i>Ind. Med. Plants</i> , Part I, 1918, 575. |
| 2. Greshoff | .. <i>Ber.</i> , 1890, 23 , 3537. |
| 3. Panse and Paranjpe | .. <i>Rasayanam</i> , 1941, 1 , No. 7, 215. |
| 4. Salkowski | .. <i>Ber.</i> , 1891, 24 , 2724. |
| 5. Paterno and Spica | .. <i>Ibid.</i> , 1876, 9 , 81. |
| 6. Werner | .. <i>Jl. Chem. Soc.</i> , 1891, 59 , 408. |
| 7. Curtius and Lederer | .. <i>Ber.</i> , 1886, 19 , 2463. |
| 8. Cannizzaro | .. <i>Ann.</i> 1855, 96 , 247. |
| 9. Purgotti | .. <i>Gaz. Chim. Ita.</i> , 1890, 20 , 173, 593, Anm. 2, quoted from Beilstein. |
| 10. Hoogewerff and van Dorp | <i>Res. des tra. chim.</i> , 1886, 5 , 253, quoted from Beilstein. |

CHEMICAL COMPOSITION OF *CALOTROPIS GIGANTEA*

Part I. Wax and Resin Components of the Latex

BY P. BHASKARA RAMA MURTI* AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair)

Received August 25, 1943

Calotropis gigantea is a shrub common in the eastern and southern parts of India, Ceylon and Eastern Asia. The milky juice obtained from it is used for medicinal and insecticidal purposes and frequent cases of criminal poisoning by its means are known. The possibilities of obtaining a guttapercha-like solid from this latex have also been considered in the past. Its chemical composition was first investigated by Basu and Nath¹ who employed the dried latex. From the unsaponifiable portion of the ether-soluble matter they isolated, after repeated purification, a product which was considered by them to be a sterol of the formula $C_{28}H_{44}O$. It was named calosterol. They, however, noted that this substance did not form a precipitate with digitonin and in most of its reactions differed from ordinary sterols. As part of their investigations on African arrow poisons G. Hesse and co-workers² examined the mixed latex obtained from *Calotropis procera* and *Calotropis gigantea*. From the alcohol-soluble portion were obtained usharin, calotoxin and calactin which belong to the group of cardiac poisons.

Considerable quantities of the latex can be collected easily and the material is best preserved by adding a little chloroform. Some amount of preliminary investigation had to be done in order to work out the most suitable method of separating the components. The procedure adopted by Basu and Nath of drying the whole material so as to obtain a solid does not seem to be satisfactory, since it leads to undesirable decompositions and the separation of the various components from the resulting product is also difficult. Coagulation by simple heating or by treatment with acids with a view to separate fractions is better, but still not adequate. The most satisfactory procedure is to add enough alcohol to produce a filterable precipitate and a clear filtrate, and it renders the separation of the various components more easy. The soft coagulum (I) and the aqueous alcoholic solution (II) were separately examined.

* At present working in the Laboratories of the Board of Scientific and Industrial Research, Delhi.

The coagulum (I) was repeatedly extracted with boiling alcohol and subsequently with ether. It was finally separated into a sticky solid (I *a*), which was difficultly soluble in ordinary solvents and which is still under investigation and a portion easily soluble in ether (I *b*). The above separation rendered the study of the ether-soluble fraction more easy. This was a crystalline solid melting between 120° and 170°. With a view to understand the nature of the components present, colour reactions were carried out using several reagents. The most characteristics reactions were a deep pink colour with the Liebermann-Burchard reagent and a yellow solution with the Salkowski reagent and these indicated the presence of triterpene compounds. With a view to obtain some information about the exact condition in which these compounds occur and if possible to obtain a pure substance repeated crystallisation was carried out. A small amount of a fraction melting at 248–50° (solid A) could be isolated; it will be described later on. The remaining portion was, therefore, subjected to saponification and the unsaponifiable matter and the fatty acids analysed separately.

The unsaponifiable matter was a pale yellow solid and consisted mostly of resinols. It was divided into two fractions using solubility in alcohol: less soluble (B) and more soluble (C). Since no definite entity could be obtained from them by adopting methods of crystallisation, they were independently subjected to acetylation and benzylation and these esters were subsequently subjected to fractional crystallisation. Such a procedure has yielded very good results in the hands of Heilbron and co-workers in similar cases. The existence of α - and β -amyriols and of lupeol in the waxy portion of *Decalepis Hamiltonii* and *Hemidesmus indicus* could be established by adopting this technique.³ By the acetylation of (B) and crystallisation of the mixed acetates using ethyl acetate a definite compound melting at 250–51° could be obtained as the major product. Its sparing solubility was noteworthy; its crystal structure (elongated hexagonal plates) was very characteristic and was very sensitive to the presence of impurities; $[\alpha]_D^{32}, +98.0^\circ$ in benzene solution. With Liebermann-Burchard reagent it produced a pink solution which deepened slowly to purple. The colour faded very slowly and after several hours it appeared to be pale blue and eventually turned yellowish brown. With Salkowski's reagent it produced a yellow solution exhibiting powerful green fluorescence. These colour reactions seemed to be individual characteristics of the substance and also indicated that it belongs to the triterpene group. This surmise was supported by the results of combustion analysis which corresponded to the formula, $C_{32}H_{62}O_2$ and by a molecular weight determination. The latter value was obtained by employing the

saponification equivalent, since it could not be correctly obtained by the camphor method of Rast. Hydrolysis of the acetate gave rise to an alcohol melting at $204-5^{\circ}$ $[\alpha]_D^{32}, +102.0^{\circ}$ in benzene solution and its composition corresponded to the formula, $C_{30}H_{50}O$. It formed no combination with digitonin. Since it did not appear to be identical with any known compound it has been given the name, α -calotropeol indicating its isolation from *Calotropis*. Its benzoate melted at $273-74^{\circ}$, $[\alpha]_D^{32}, +74.3^{\circ}$ in benzene solution. Thus the alcohol and its esters are all dextro-rotatory. From a determination of the iodine value of the acetate the presence of one double bond in the compound could be established. From the mother liquors left after the separation of α -calotropeol-acetate, small quantities of the acetates of another new alcohol, β -calotropeol (see below) and of β -amyrin could be obtained with great difficulty. However, β -calotropeol was more easily obtained in good quantity as its benzoate from the crystallisation of the mixed benzoates produced by the benzylation of the original resinol mixture (B).

By the repeated crystallisation of the mixed benzoates a substance melting sharp at $279-80^{\circ}$ could be isolated. It was different from α -calotropeol benzoate, the mixed melting point being depressed and its specific rotation, $[\alpha]_D^{32}, +69.0^{\circ}$ in benzene solution was also different thus showing that they are different substances. However, from combustion analysis and molecular weight determination it was found to be isomeric. The free alcohol obtained from it melted at $216-17^{\circ}$ and had the specific rotation, $[\alpha]_D^{32}, +50.9^{\circ}$ in benzene solution and was thus different from α -calotropeol. It was, therefore, named β -calotropeol. It resembled α -calotropeol in its composition and colour reactions. The individuality of β -calotropeol was further supported by the preparation of the acetate which was found to melt at 238° , $[\alpha]_D^{32}, +43.9^{\circ}$, and to be quite different from α -calotropeol acetate, the mixed melting point being depressed. It should be mentioned here that the calotropeols were found to be stable and their acetates did not undergo any change on boiling with formic acid.

The more soluble fraction (C) of the unsaponifiable matter was similarly analysed. The acetate method seemed to be the most satisfactory in this case and by the crystallisation of the crude acetates, a pure substance melting sharp at $239-40^{\circ}$ could be isolated. It had the formula, $C_{32}H_{52}O_2$ and gave colour reactions characteristic of pentacyclic triterpenes. On hydrolysis it yielded an alcohol melting at $196-97^{\circ}$. The acetate and the alcohol were found to be identical with β -amyrin acetate and β -amyrin respectively by comparison with authentic samples obtained from the roots of *Decalepis Hamiltonii*. The more soluble portion of the acetates yielded finally a fraction

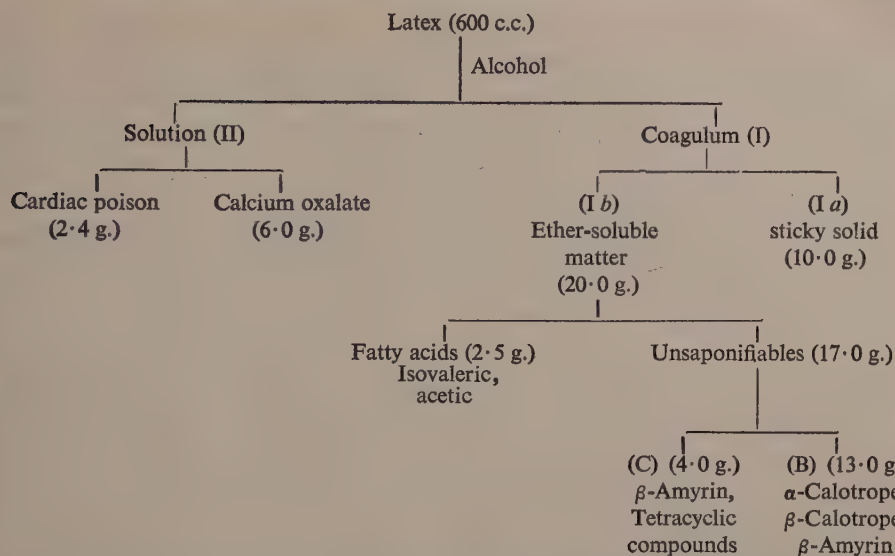
melting at 172–74° and its composition corresponded to the formula, $C_{32}H_{52}O_2$. It was dextro-rotatory. The colour reactions, however, were different from those of the above compounds; with both the Liebermann-Burchard and Salkowski reagents it produced yellow solutions with green fluorescence. This fraction seemed, therefore, to contain tetracyclic triterpenes and this surmise was confirmed by treatment with formic acid or with chloroform saturated with hydrogen chloride. The new product melted between 211 and 215° and gave the colour reactions of the pentacyclic triterpenes (similar to β -amyrin). Thus the presence of mixtures of β -amyrin and tetracyclic resinols was established.

By the decomposition of the soap obtained from the saponification of the ether-soluble portion of coagulum (I) were produced only steam-volatile fatty acids. The existence of acetic acid and of isovaleric acid in the mixture was indicated by the lanthanum nitrate test⁶ for the former and the characteristic smell of the latter. An artificial mixture of the two acids could be prepared having practically the same smell as the steam-volatile acids obtained from the latex.

Summing up the results, the ether-soluble portion of the coagulum consists of the esters of triterpene alcohols (acetates and isovalerates). α - and β -calotropeols occur in equal amounts and they form the major portion; β -amyrin comes next and small amounts of tetracyclic compounds also seem to exist.

The aqueous alcoholic solution (II) left after the separation of the coagulum contained substances which could be extracted by means of ether and chloroform. These, after purification using chloroform and petroleum ether, yielded a colourless crystalline substance (mixture of compounds) melting at about 242°. Its colour reactions and solubility indicated that it was not a wax component but belonged to the group of cardiac poisons described by Hesse *et al.* This mixture was highly toxic to fish, gave tests for N and S indicating that compounds containing these elements were present. Further study of this material is in progress. The aqueous alcoholic solution from which all ether- and chloroform-soluble matter had been removed, deposited slowly a colourless solid, and this was identified as calcium oxalate by qualitative and quantitative analyses and examination of its crystalline structure. It is probable that the irritating effect of the latex when rubbed on the skin is due to the presence of this substance in a very fine crystalline condition. This phenomenon has been noticed in some other cases, one such being *Vitis quadrangularis*.⁴

The following chart embodies in brief the isolation of the various fractions and their compositions.



As already mentioned Basu and Nath investigated the ether extract of the dried latex and claimed to have obtained as the sole crystalline component of the unsaponifiable matter a new sterol called calosterol. Though its reactions were abnormal for a sterol they seem to have been led to this opinion by the formula, $C_{28}H_{44}O$ that they obtained for it. However, the carbon analysis of calosterol and of its acetate and benzoate agree closely with the values required for the monohydric triterpene alcohols, $C_{30}H_{50}O$ and their derivatives, though the recorded hydrogen values of the former are low all through. From the results of the present work and particularly from a comparison of the melting points it seems to be quite possible that the above authors were dealing with a mixture of resinols. It was probably contaminated with cardiac poisons since these are also soluble in ether and would get into the ether extract when the whole of the latex in a dry condition is extracted. The cardiac poisons give an immediate green colour with the Liebermann-Burchard reagent and their presence might have contributed to the colour changes observed with calosterol when treated with this reagent.

It may be mentioned in this connection that the latex of another species of *Calotropis*, *Calotropis procera* has been recently analysed by Hesse⁵ *et al.* and has been found to contain a triterpene alcohol. From the abstract of the paper which alone is now available it could be seen that the sole alcoholic component of the latex is α -lactuceryl. It has a melting point of $224-25^\circ$, $[\alpha]_D^{20} + 97.5^\circ$ and its acetate and benzoate melt at 252° and 257° respectively. On boiling with formic acid it isomerises to iso-lactuceryl melting at 201° ; $[\alpha]_D^{20} + 66.8^\circ$. The acetate and benzoate of iso-lactuceryl melt

at 237° and 271° respectively. The alcohols are given the formula $C_{30}H_{50}O$ and they produce colour reactions similar to those noted for the calotropeols. They are described as pentacyclic triterpene alcohols. These observations are in accord with the results of the present investigation of the latex of *Calotropis gigantea*, that the components are resinols though the compounds present in the two species are different. They further support the conclusion that 'calosterol' should be considered to be a mixture of triterpene alcohols.

With regard to the composition of the latex of *Calotropis procera* Hesse *et al.* found it to contain (1) cardiac poisons and (2) esters of α -lactuceryl with steam-volatile fatty acids. The present investigation shows that the latex of *Calotropis gigantea* contains (1) cardiac poisons, (2) esters of α - and β -calotropeols and β -amyrin with steam-volatile fatty acids and (3) calcium oxalate. Besides others the most characteristic difference between α -lactuceryl and the resinols of *C. gigantea* is that the former undergoes isomeric change when treated with formic acid, whereas the latter are stable to such treatment.

Experimental

Fresh latex was collected in bottles containing a few drops of chloroform. In order to bring about coagulation of colloidal matter, it (600 c.c.) was treated with rectified spirits (200 c.c.), the mixture was well stirred and set aside for some hours. The coagulum (I) (35.0 g.) was separated from the aqueous alcoholic mother-liquor (II) by filtration under gentle suction and the two were examined separately.

The soft coagulum (I) was boiled with alcohol (500 c.c.) under reflux, filtered and the extraction repeated twice again using 250 c.c. of alcohol each time. The residue was then extracted repeatedly with boiling ether till no more went into solution. A small sticky portion (I a), pale yellow in colour was left behind; it was difficultly soluble in ordinary solvents, contained a little mineral matter and gave tests for phosphate. The combined alcoholic extract deposited on standing a bulky solid which was completely soluble in ether. It closely resembled the ether extract and was therefore added to it (I b). On evaporating the clear alcoholic solution a yellowish brown sticky solid was obtained. It resembled (I a) closely and the two were mixed together (10.0 g.). This is under further investigation.

Ether solution, (I b) (Resinol esters, 20 g.).—On distilling off the solvent completely the dry residue was obtained as a colourless, non-sticky solid

melting indefinitely between 120° and 170°. To effect, if possible, the isolation of pure compounds by direct crystallisation, it (25.0 g.) was dissolved in boiling ethyl acetate (300 c.c.) and the solution was left undisturbed for about 6 hours. A glistening mass of colourless crystals melting at 210–15° separated out. Two more crystallisations of this solid (5.0 g.) from the same solvent yielded a product melting at 230–35°. Further repeated crystallisation using ether and ethyl acetate alternately left a small amount of (0.5 g.) of a pure product melting at 248–50° (A). Description of this substance has been postponed for the present.

All the impure fractions were mixed together. The solid (20.0 g.) was dissolved in benzene (200 c.c.), N/2 alcoholic potash (500 c.c.) added and the contents were boiled under reflux for 15 hours. By this time a large amount of a crystalline solid (needles) was found to separate out. The solvents were removed by distillation as far as possible, water was added to the residual mixture and boiled. The unsaponifiable matter was isolated by ether extracting the aqueous suspension; during this operation no emulsions were formed and the soap solution remained clear all the time.

Fatty acids (acetic and isovaleric acids).—Before decomposing the soap solution with acids the last traces of alcohol were carefully removed by heating under reduced pressure. This precaution is necessary, since lower fatty acids readily form volatile esters with alcohols in the presence of mineral acids and thus give rise to complications. The acidified solution did not form any layer of insoluble fatty acids and hence the clear solution was subjected to steam distillation. The distillate (2 litres) was ether extracted, the extract dried over anhydrous sodium sulphate and finally distilled to recover the solvent. The liquid residue was strongly acidic in reaction and had an offensive smell. Treatment with lanthanum nitrate⁶ produced a blue solution indicating the presence of acetic acid and the smell was characteristic of isovaleric acid. Careful comparison of the odour of a dilute solution of the mixed fatty acids with a similar solution containing authentic samples of acetic and isovaleric acids confirmed the presence of these two acids in the mixture.

The residue in the distilling flask was a clear solution. It was repeatedly extracted with ether and the ether solution evaporated. The absence of any residue showed that solid and liquid non-volatile fatty acids were absent.

Unsaponifiable matter, Resinols (17.0 g.).—The ether solution of the unsaponifiable matter was distilled in order to remove the solvent completely. The residue (17.0 g.) was a pale yellow solid containing some colourless crystals. It was readily soluble in benzene, ethyl acetate and

ether, but was much less soluble in both methyl and ethyl alcohols. When the whole solid was boiled under reflux with rectified spirits (400 c.c.) and the contents allowed to stand overnight a crystalline solid (B) separated out. It was filtered off and the alcoholic filtrate concentrated in stages. Since no more crystalline solid could be obtained by this process, the whole of the filtrate was evaporated to dryness and the residue (C) was separately examined.

Solid (B) (13.0 g.), α - and β -calotropeols and β -amyrin.—This fraction crystallised from alcohol in long colourless needles melting at 120–70°. Simple crystallisation from ordinary solvents a number of times did not yield sharp melting substances. Consequently esters (acetate and benzoate) were prepared and studied.

Acetate method (α -calotropeol acetate).—The resinol mixture (8.0 g.) was dissolved in acetic anhydride (20 c.c.), anhydrous sodium acetate (5.0 g.) was added and the mixture was kept boiling under reflux for 3½ hours in an oil-bath. It was cooled, diluted with water (300 c.c.) and kept in the ice-chest overnight. The separated solid was extracted first with excess of boiling ether and subsequently with boiling benzene. Only a little dark resinous matter was left behind and it was discarded. Both the ether and benzene solutions were decolourised by warming with 'norit' and concentrated independently. They yielded the same crystalline solid melting at about 230° which when recrystallised from ethyl acetate melted at 240–44°. The two fractions from the two solvents were mixed together and twice crystallised from ethyl acetate when a compound melting at 250–51° was obtained (0.5 g.).

The crystal structure was quite characteristic; the compound came out slowly in the form of glistening, elongated hexagonal prisms. It was very sparingly soluble in both ethyl and methyl alcohols, moderately soluble in ether and ethyl acetate and readily soluble in chloroform and benzene. With Liebermann-Burchard reagent it produced a pink solution which very slowly faded to a yellow brown. With the Salkowski reagent it formed a yellow solution exhibiting green fluorescence. Treatment with boiling formic acid did not produce any change. [Found: C, 82.5; H, 11.2; $C_{32}H_{52}O_2$ requires C, 82.1; H, 11.1%]. $[\alpha]_D^{30}, +98.0^\circ$ in benzene solution. The molecular weight of the acetate was determined by finding the saponification equivalent. The solid was dissolved in benzene, excess of N/2 alcoholic potash was added to it and the contents were boiled under reflux for 3 hours. A blank experiment was conducted simultaneously. The unused alkali was estimated by titration with standard acid. The molecular

weight was found to be 462 and that required for the formula given above is 468. The iodine value was determined as follows: The substance (0.2180 g.) was dissolved in carbon tetrachloride (20 c.c.), an equal amount of iodine chloride solution was added and the contents were kept in the dark for 3 hours. The excess of iodine was then titrated in the usual way with sodium thiosulphate. The I. V. obtained was 57.4 and that required for one double bond in the above formula 54.2.

α -Calotropeol.—The acetate (2.0 g.) was dissolved in benzene (50 c.c.), an equal amount of 5% alcoholic potash was added to it and the mixture was boiled under reflux for 5 hours. The major bulk of the solvents was distilled off and the residue was diluted with water. The resulting solid was washed free of alkali and dried. It was dissolved in a mixture of boiling acetone (125 c.c.) and ether (20 c.c.) and allowed to crystallise slowly in the refrigerator. A good amount of crystalline solid was collected at the bottom of the flask and was recovered by filtration. It appeared as transparent rods and narrow plates under the microscope and melted at 204–5°. It resembled the acetate in its solubility in the ordinary organic solvents except benzene in which it was more sparingly soluble. It gave a bright pink solution immediately with the Liebermann-Burchard reagent; the colour changed to purple in about an hour; after 2 hours it was pale blue and slowly faded to yellowish brown (5 hours). These changes could be brought about rapidly by the addition of a few drops of water. With the Salkowski reagent the sulphuric acid layer was coloured orange-yellow exhibiting deep green fluorescence. [Found: C, 84.6; H, 11.4; $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%]. $[\alpha]_D^{20}$, +102.0° in benzene solution.

Benzoate of α -Calotropeol.—The crystalline alcohol (0.6 g.) was dissolved in benzene (40 c.c.) and pyridine (8 c.c.) and benzoyl chloride (7 c.c.) were added to it. The mixture was set aside for 12 hours and then heated under reflux for 3 hours on a water-bath. The solvents were removed under low pressure and the resulting residue was dissolved in ether-benzene mixture (150 c.c.). The solution was washed with 1% sodium hydroxide solution followed by aqueous sulphuric acid. Finally it was washed free of acid with water. It was dried over anhydrous sodium sulphate and gently warmed to remove the ether as far as possible. To the concentrate (20 c.c.) an equal amount of alcohol was added and the mixture was allowed to cool slowly. A crystalline solid melting at 273–74° was obtained and no change in the melting point was effected by crystallising it from ligroin (20 c.c.). It crystallised in the form of broad rectangular plates. [Found: C, 83.6; H, 9.8; $C_{37}H_{54}O_2$ requires C, 83.8; H, 10.2%]. $[\alpha]_D$, +74.3° in benzene solution. It gave the same colour reactions as the acetate.

Isolation of acetate of β -calotropeol and β -amyrin.—The ethyl acetate mother-liquor left after removing the acetate of α -calotropeol was concentrated and the earlier fractions which were mixtures of this compound were removed. Later a small fraction melting at 232–35° was obtained. Repeated recrystallisation of this from ethyl acetate yielded a product melting at 238–39° which proved to be identical with β -calotropeol acetate (see below). Though the existence of β -calotropeol in the resinol mixture was thus indicated, its isolation in larger quantities was conveniently effected by the benzoate method.

The final ethyl acetate filtrates from which the acetates of the calotropeols had been separated and the original ether and benzene mother-liquors were all united, evaporated to dryness and the residue carefully studied. It (4.0 g.) was dissolved in ether (150 c.c.), an equal amount of alcohol was added and the contents were stirred well. Immediately a solid melting at 205–8° and containing acetates of calotropeols separated out; it was removed by filtration. The mother liquor was concentrated in stages and five fractions were collected. The first of these melted between 173–85° and the last 90–135°. The last two fractions were coloured yellow. By fractionation of these several times from acetone and ethyl acetate, a small amount of a solid melting at 190–206° was collected. Further crystallisation from benzene-alcohol mixture and finally ethylacetate yielded a product melting at 239–40° and crystallising in the form of long prismatic rods. It produced a pink solution with the Liebermann-Burchard reagent and no change in the colour was effected by the addition of water; with the Salkowski reagent a yellow solution was formed. It was different from the acetates of the calotropeols and the mixed melting points with these compounds were considerably depressed. From its properties it appeared to be β -amyrin acetate and this surmise was proved to be correct by a mixed melting point determination using an authentic sample of β -amyrin acetate obtained from the roots of the *Decalepis*. On hydrolysis it yielded β -amyrin.

Benzoate method (β -calotropeol benzoate).—Solid (B) (5.0 g.) was dissolved in benzene (30 c.c.), benzoyl chloride (12 c.c.) and pyridine (10 c.c.) were added and the contents were set aside for 12 hours. Then the mixture was heated on a water-bath for 5 hours. The solvents were removed completely under low pressure and the residue was taken up with water. The aqueous suspension was extracted with a mixture of ether and benzene (2:1), (300 c.c.) in small lots and the ether-benzene layer was washed with 1% aqueous sodium hydroxide, dilute sulphuric acid and water in succession. The solution on concentration to about 100 c.c. deposited a solid (3.0 g.) melting at 200°. It was digested with ether (100 c.c.) and the ether-insoluble

portion was carefully separated by decanting off the solution. On crystallisation from a mixture of benzene and alcohol (50 c.c.) it yielded a fraction (0.8 g.) melting at about 260°. Further purification of the solid was effected by dissolution in petrol (50 c.c.) and cooling the solution in ice after concentrating to half the bulk. As a result a solid (0.4 g.) melting at 274–77° separated out and after one more crystallisation from the same solvent it was obtained as long rectangular plates melting at 279–80°. No more rise in the melting point could be effected by further purification. With the resinol colour reagents it reacted to produce coloured solutions similar to those given by α -calotropeol and its derivatives. [Found: C, 83.7; H, 10.4; $C_{37}H_{54}O_2$ requires C, 83.8; H, 10.2%.] $[\alpha]_D^{33}, +69.0^\circ$ in benzene solution. The molecular weight determined as already described by finding the saponification equivalent was 538, the value required for the above formula being 530. The mixed melting point with α -calotropeolbenzoate was considerably depressed.

β -Calotropeol.—The benzoate (0.8 g.) was dissolved in benzene (45 c.c.) and the solution was boiled with an equal amount of N/2 alcoholic potash for 5 hours. The major bulk of the solvents was distilled off and the residue was treated with water. The resulting solid (β -calotropeol) was filtered and washed free of alkali. It melted at 216–17°, after a crystallisation from benzene-alcohol mixture (2:1). On concentrating the mother-liquor in stages, only the above substance could be obtained. The alcohol as well as the benzoate were thus shown to be pure. The mixed melting point with α -calotropeol was found to be depressed (175–95°).

β -Calotropeol appeared as prismatic rods under the microscope. It was practically insoluble in alcohol and readily dissolved in ether, chloroform and benzene. In the last solvent its solubility was less than that of its acetate (see below). It produced the same colour reactions with the Salkowski and the Liebermann-Burchard reagents as α -calotropeol. [Found: C, 84.7; H, 11.2; and $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%.] $[\alpha]_D^{32}, +50.9^\circ$ in benzene solution. [Found: iodine value, 57.8; $C_{30}H_{50}O$ requires for one double bond, 59.6].

β -Calotropeol Acetate.— β -Calotropeol (0.5 g.) was dissolved in acetic anhydride (10 c.c.), a few drops of pyridine were added and the solution boiled for 3 hours. On adding water and allowing the contents to stand overnight the acetate separated out as a colourless solid. It was crystallised from ethyl acetate (20 c.c.) and the resulting crystalline compound melted at 238°. Under the microscope it appeared as elongated hexagonal plates. When crystallised from benzene-alcohol mixture, it was obtained as a woolly

crystalline mass and it appeared as thin rods under the microscope. It was easily soluble in benzene and chloroform, moderately soluble in ether and ethyl acetate and practically insoluble in ethyl and methyl alcohols. It produced the same colour reactions as the benzoate. The substance was unaffected when boiled with formic acid. [Found: C, 81.7; H, 10.9; and $C_{32}H_{52}O_2$ requires C, 82.1; H, 11.1%.] $[\alpha]_D^{30}, +43.9^\circ$ in benzene solution. Mixed melting point with α -calotropeol acetate was found to be depressed (225–230°).

When the mother-liquors from the crystallisation of the benzoate mixture were worked up some more of the β -calotropeol benzoate could be obtained and it was not possible to isolate α -calotropeol or β -amyrin esters.

Solid (C) (4.0 g.) (β -amyrin and tetracyclic compounds).—It was yellow in colour and sticky to the touch and was found to be soluble in all organic solvents making purification by crystallisation difficult. From its colour reactions it was considered to consist mostly of resinols. To facilitate the isolation of crystalline products it was studied by the acetate method. Its acetylation was carried out in the usual way by boiling the solid (4.0 g.) with acetic anhydride (15 c.c.) in presence of sodium acetate for 3 hours. The mixture was diluted with water and after allowing to stand for some hours it was ether extracted. On concentrating the ether solution to about 30 c.c. a crystalline solid mixed up with an yellow amorphous substance separated out. Repeated washing with small quantities of ether removed the coloured portion leaving behind colourless crystals melting at 218–30°. Two more crystallisations of the above fraction (1.5 g.) from ethyl acetate resulted in the separation of a colourless crystalline compound melting sharp at 240°. It was identified as β -amyrin acetate by making a mixed melting point determination with an authentic sample.

The ether mother-liquor and washings, on careful concentration in stages, deposited some more of crude amylin acetate. The final solution was evaporated almost to dryness when a residue was obtained in the form of a thick syrup. It was shaken well with acetone (30 c.c.) and on allowing the contents to stand for about 6 hours a colourless solid melting at 148–60° was deposited. The mother-liquor on careful manipulation yielded some more of the above solid. On crystallisation from acetone it was obtained in the form of broken cubes and it melted at 170–74°. Further purification was not attempted since the yield of the substance was only 0.5 g. [Found: C, 82.6; H, 11.2; $C_{32}H_{52}O_2$ requires C, 82.1 and H, 11.1%]; $[\alpha]_D^{30}, +44.0^\circ$ in benzene solution. It differed from β -amylin acetate in producing a yellow solution exhibiting green fluorescence with Liebermann-Burchard

reagent in place of a pink coloured solution. This property was made use of in the above fractionation to detect and eliminate β -amyrin acetate which if present even in traces would invariably produce the pink solution. With the Salkowski reagent it produced a yellow solution with green fluorescence. The low melting point of the acetate coupled with the colour reactions indicated that it was probably a tetracyclic resinol mixture. This surmise was confirmed by effecting ring closure by the following two methods: Formic acid (20 c.c.) was added to the benzene solution (20 c.c.) of the substance and the mixture was boiled for 3 hours. The contents were largely diluted with water and the benzene layer was separated, washed free of acid and was concentrated to about 5 c.c. On the addition of an equal volume of alcohol and cooling the solution in ice, a crystalline solid melting at about $211-15^{\circ}$ was obtained. This produced the characteristic colour reaction of the pentacyclic triterpenes, *i.e.*, pink solution with the Liebermann-Burchard reagent. However, the benzene-alcohol mother-liquor from the above compound yielded on evaporation a large amount of the unchanged original compound. This was dissolved in chloroform (15 c.c.), the solution was saturated with dry hydrogen chloride at 0° C. and kept at that temperature overnight. The residue obtained after removing the solvent was crystallised from benzene-alcohol and ethylacetate in succession resulting in the isolation of the transformation product in a better yield.

The final mother-liquors left after removing the crude tetracyclic compounds were examined in detail to see if any sterol-like substances could be detected. No fraction gave the proper sterol colour reactions when tested with the Liebermann-Burchard and Salkowski reagents. Solid (C) thus consisted mostly of β -amyrin and small quantities of tetracyclic compounds.

Filtrate (II) (Cardiac poisons and calcium oxalate).—The filtrate obtained from the coagulum (I) on cooling in the refrigerator deposited only a small amount of a slimy solid. Hence the whole solution was extracted repeatedly with ether employing 500 c.c. of it at a time. The ether solutions were united and extracted with 5% aqueous sodium carbonate twice. The ether layer was washed free of alkali and dried over anhydrous sodium sulphate; on distilling off the solvent it left behind a residue melting at about 235° . It was further purified by dissolving in chloroform (100 c.c.) and reprecipitating by the addition of petrol (500 c.c.). The purified solid (0.4 g.) was obtained in the form of colourless rods and melted at $241-43^{\circ}$. It produced a green solution with the Liebermann-Burchard reagent and the colour of the solution changed to red after a day. It dissolved in strong hydrochloric acid producing a greenish blue solution. It tasted bitter leaving a tingling sensation on the tongue.

The carbonate solution was acidified with hydrochloric acid and was slightly warmed, when an offensive smell emanated. The acid solution was repeatedly ether extracted and all the ether solutions were united. The solvent was completely removed by distillation and the residue was dissolved in chloroform and reprecipitated by the addition of petroleum ether. The resulting product was very small and was not further studied.

The original filtrate (II) which had been extracted with ether, was extracted with chloroform in four lots employing 400 c.c. of chloroform each time. All the chloroform solutions were mixed and the solution was concentrated to about 25 c.c. No solid separated out even on prolonged cooling in the refrigerator. Then about 100 c.c. of petrol were added and the contents were well stirred when a solid slowly began to separate out. It was crisp and it melted at about 220° (yield 2.0 g.). It gave colour reactions very similar to those of the compound melting at 241° . They were both toxic to fish and in general resembled usharin and related compounds isolated by Hesse *et al.* from the mixed latex obtained from *Calotropis procera* and *gigantea*. No further detailed study was made of them.

After the filtrate (II) had been extracted with chloroform and the chloroform layer removed, a small quantity of an insoluble compound slowly began to separate out from the aqueous layer. It was found to be insoluble in alcohol also. Making use of this property, the substance could be completely separated from the aqueous solution by adding a liberal quantity of alcohol (600 c.c.) and leaving the contents undisturbed for a week. A sticky solid thus precipitated down at the bottom of the flask and was filtered at the pump. Further purification was effected by digestion with alcohol (500 c.c.) whereby it was obtained as a non-sticky solid (6.0 g). It neither melted nor burnt when introduced into a flame and hence was considered to be an inorganic salt. Further it was not soluble in any organic solvent or in water. In acetic acid medium it appeared as plates and bunches of needles under the microscope. Its resemblance in crystalline structure to an authentic sample of calcium oxalate was very marked. Further on ignition calcium oxide was obtained in quantitative yield. It readily dissolved in hot dilute sulphuric acid and the solution reduced potassium permanganate. From the above properties it was identified as calcium oxalate and its estimation was carried out by permanganate titration. Most of the solid (95%) was found to be calcium oxalate, the yield being 1% on the weight of the latex.

The aqueous alcoholic solution was concentrated to about 500 c.c. and was treated with hot neutral and basic lead acetate solutions in succession. The insoluble lead salts were collected and decomposed separately in the

usual way by passing hydrogen sulphide through the aqueous suspensions. After removing the lead sulphide the filtrates were extracted with ether and chloroform in succession. From the ether solution only a small quantity of a crystalline resin acid melting at 135° could be obtained. From the chloroform solution no compound could be obtained; all the chloroform-soluble substances had obviously been removed earlier. The aqueous filtrate on further concentration and hydrolysis with aqueous sulphuric acid yielded amorphous resins.

Summary

The latex of *Calotropis gigantea* contains (1) resinols as esters of steam-volatile fatty acids (acetic and isovaleric), (2) cardiac poisons similar to usharin and (3) calcium oxalate. The resinol portion consists mainly of two new alcohols, α -calotropeol and β -calotropeol in almost equal quantities and minor amounts of β -amyrin. The important properties of the calotropeols have been studied. It is suggested that 'Calosterol' of Basu and Nath should be a mixture of resinols contaminated with cardiac poisons. The recent report of Hesse *et al.* that the milky latex of *Calotropis procera* contains only α -lactuceryl as its esters with steam-volatile fatty acids is discussed.

REFERENCES

1. Basu and Nath .. *Biochem. J.*, 1924, **28**, 1561.
2. Hesse *et al.* .. *Ann.*, 1939, **537**, 67-86.
3. Murti and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1941, **14**, 93.
4. ————— .. *Ibid.*, 1939, **9**, 121.
5. Hesse *et al.* .. *Ann.*, 1941, **546**, 233 ; *B. C. A.*, 1942, **A 2**, 43.
6. Neelakantam and Row .. *Proc. Ind. Acad. Sci. (A)*, 1941, **13**, 194.

FIXED OIL FROM *JATROPHA CURCAS* (LINN.)

BY A. R. SUKUMARAN KARTHA AND K. N. MENON

(Maharaja's College, Ernakulam)

Received July 24, 1943

Jatropha curcas or the angular-leaved physic nut flowers in May-June and the fruits ripen during the monsoon. The oil from the seeds has been analysed by many investigators and only two have published complete analysis of the component acids, the others only separating the solid and liquid acids and in some cases determining the proportion of the oleic and linoleic acids in the latter. Kajuka, Hata and Fujikawa¹ gave the component acids of the Formosan oil, of iodine value 130, as 14.4% palmitic, 9.6% stearic, 53.2% oleic and 22.8% linoleic acid. These results are not in agreement with the recorded iodine value and can be accepted only with caution. The same trouble arises in accepting the values recorded by Cruz and West.²

For the present investigation the seeds were collected locally and the oil obtained shows a higher density and lower iodine value than all other samples hitherto examined. The analytical constants of the Malabar oil together with the constants of other curcas oils are shown in Table I. The mixed acids (96.4%) gave 24.57% of solid acids and 75.43 of liquid acids. Complete analysis has shown that the constituent acids are myristic 1.37%, palmitic 15.61%, stearic 9.69%, arachidic 0.35%, oleic 40.9% and linoleic 32.08%. The Euphorbiaceæ oils in general contain only very small amounts of saturated acids and *Jatropha* oil is the first in the whole of the family which has been shown to contain more than 18% of saturated acids. The component acids of some typical Euphorbiaceæ fats are shown in Table II for comparison.

The component glycerides of Euphorbiaceæ have received very little attention. Hilditch and Priestman³ records the glyceride composition of the fruit coat fat of *Stillingia sebifera*, and the present is the first report on the glyceride composition of the seed fat in this group. The analysis of the azelao glyceride mixture has already been published⁴ and in this paper the data relating to the trisaturated glyceride content is reported. It is interesting to note that this oil does not obey the rule of even distribution.

The studies of Ivano and others⁵ have resulted in the conclusion that a given plant species, capable of existence in different climates, produces, when

TABLE I

Authority	Density	Refr. Index	Acid Value	Sapon. Value	Iod. Value	Unsataponified %	Locality
Siam Govt. Laboratory { (1)	0.924	1.4640	7.5	192.6	101.1	..	Siam
Kinzo and Chinta { (2)	0.923	1.4623	12.84	202.9	98.2	..	Do.
Simon et Droit { (3)	0.9152	1.4695	2.86	195.22	102.31	1.25	Formosa
{ (4)	..	1.4720	6.4-9.6	188-190	93.00	..	Barbadoes
{ (5)	..	1.4730	4.8	176-180	97.98	..	Do.
{ (6)	0.9168	1.4720	4.5-5.5	176.00	93.00	..	Do.
{ (7)	0.9205	1.4733	4.0-9.6	190.00	98.00	..	Do.
{ (8)	0.9106	1.4722	38.68	196.32	106.90	1.15	Belgian Congo
L. A. Drians { (9)	0.9219	2.91	5.10	193.20	96.20	0.50	Do.
Cruz and West { (10)	0.9820	1.4665	26.27	192.40	94.80	0.45	Philippine
Present work { (12)	0.9849	1.4669		196.10	90.84	0.20	Malabar

TABLE II. Component Acids of the *Euphorbiaceæ*

No.	Name	C ₁₈	C ₁₈	Ol	Linol.	Others	Authority
1	<i>Aleurites cordate</i>	..	1.3	6.5	19.4	74.1 Elæo-stearic	Mc. Kinney and Jameson ¹
2	<i>Croton tiglium</i>	55.8	11.3 C ₁₄ and 2.3 C ₂₀ acids	Flaschentrager and Wolffersdorff ²
3	<i>Euphorbia lathyris</i>	..	8.3	5.8	91.9	2.3 Linolenic	Zoleol ³
4	<i>Hevea brasiliensis</i>	23.6	43.3	Griffiths and Hilditch ⁴
5	<i>Ricinus communis</i>	17.0	12.0	Steger and Van Loon ⁵
6	<i>Stillingia sebifera</i>	..	4.7	10.4	7.2	11% linolenic	Panjutin and Rapport ⁶
7	<i>Jatropha curcas</i>	..	15.61	..	8.1	Ricinoleic	Jameson and Mc. Kinney ⁷
8		40.9	25.9 Linolenic	Present work
		32.08	0.35 C ₂₀ 1.37, C ₁₄	

1. Mc. Kinney and Jameson, *Oil and Soap*, 1937, 14, 2.
2. Flaschentrager and Wolffersdorff, *Hebe. Chem. Acta*, 1934, 17, 1444.
3. Sobol and others, *Maslob. Shir. Delo*, 1935, 11, 132.
4. Griffiths and Hilditch, *J. Soc. Chem. Ind.*, 1934, 53, 75 T.
5. Steger and Van Loon, *Rec. Trav. Chim.*, 1935, 54, 988.
6. Panjutin and Rapport, *Chem. Unschan*, 1930, 37, 130.
7. Jameson and Mc. Kinney, *Oil and Soap*, 1938, 15, 295.

grown in a cold climate, more unsaturated acids in its seed fats than when it is grown in a warmer climate. A perusal of the literature connected with *Jatropha* oils shows that probably more important than the general climatic condition, the minimum temperature to which the plant is subjected, influences the degree of unsaturation of the oil. The oil of curcas from Belgian Congo, practically on the equator and subject to extremes of heat and cold, has an iodine value of 97–102, Malabar (8° N.) oil has 90·84, Philippine (15° N.) has 95·00, Formosa (23° N.) has 103·0. The Belgian Congo seeds are subjected to much greater variations in respect of heat and cold so much so that the oil shows higher unsaturation than the Malabar oil or Philippine oil, and its unsaturated nature is on a par with Formosan oil from seeds grown in a much colder climate.

Experimental

450 Grams of clear dry oil were obtained by extraction of 972 grams of the crushed seeds, and gave the following constants :—

Density (30° C.)	0·9849	Refractive Index	1·4669
Acid value	26·27	Saponification value	196·1
Acetyl value	Nil	Iodine value	90·84
Water insoluble acids	96·4%	Non-saponifiable matter	0·2%

Constants of Mixed acids.—

Titre	26°	Refractive index	1·4583
Mean Molecular weight	277·2	Iodine value	94·85

The mixed acids were separated into solid and liquid acids showing the following constants :—

(a) *Solid acids.*—(24·57% of the mixed acids).

Titre	52·5°	Mean molecular weight	268
Iodine value	0·65	Refractive index	1·4496

(b) *Liquid acids.*—(75·43% of the mixed acids).

Mean molecular weight	282·1	Refractive index	1·4650
Iodine value	117·0		

The solid and liquid acids were converted into their esters, fractionated and worked up as usual. Careful fractionations followed by hydrolysis and analysis gave the following values :—

Solid acids :—

C_{14} —0·25; C_{16} —14·11; C_{18} —9·69; C_{20} —0·35;
Oleic—0·07; Linoleic—0·10

Liquid acids :—

C_{14} —1·12; C_{16} —1·50;
Oleic—40·83 Linoleic—31·98

Thus the composition of the total acids is found to be myristic 1.37%, palmitic 15.61%, stearic 9.69%, arachidic 0.35%, oleic 40.90% and linoleic 32.08%.

Permanganate Oxidation

120 Grams of the neutral oil gave 3.41 grams of neutral non-oxidisable portion corresponding to 2.84% of saturated glycerides.

Confirmation of the above value by an independent method could not be attempted due to lack of suitable methods. The oil is miscible in all proportions with dry acetone and could not be crystallised from it. The estimation of tristearin in the completely hydrogenated fat would be useless firstly because the oil contains nearly 10% of stearic acid and secondly because it contains nearly 16% of palmitic acid. The tristearin value will thus be about 55 and it has been proved⁶ that this method is unreliable when the value lies between 40 and 75. The estimation of tri-C₁₈-glycerides by the partial hydrogenation method would not give any accurate results since the oil contains nearly 10% of stearic acid.

Summary

The constants, mixed acid composition and the trisaturated glyceride content of the oil from the seeds of *Jatropha curcas* (Linn.) are recorded.

REFERENCES

1. *J. Chem. Soc. Japan*, **53**, 1115.
2. *Philippine J. Sci.*, **61**, 437.
3. *J. Soc. Chem. Ind.*, 1930, **49**, 197.
4. *Proc. Ind. Acad. Sci.*, 1943, **17**, 114.
5. *Ber. D. Botan. Ges.*, 1926, **44**, 31 ; *Z. Angew. Chem.*, 1929, **42**, 292 ; *Chem. Umschau* 1931, **38**, 96 ; see also S. Jaschkevitch, *Fat Chem. Umschau*, 1933, **40**, 197.
6. *The Chemical Constitution of Natural Fats*, p. 194.

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XV. Condensation of 5-Bromosalicylaldehyde and of 3: 5-Dibromosalicylaldehyde: Influence of Dissimilar Groups

BY KANTILAL C. PANDYA

AND

MISS RASHMI BALA K. PANDYA

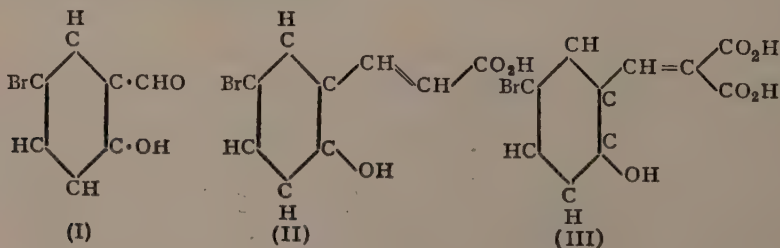
(Chemistry Laboratory, St. John's College, Agra)

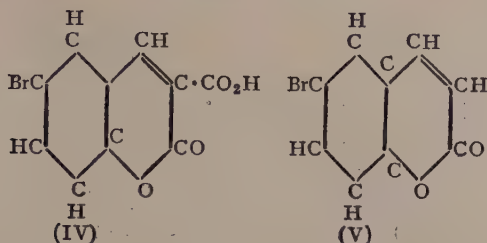
Received August 21, 1943

IN Part XIV¹ it was shown that the presence of two nitro-groups on the aromatic ring, as in 2:4-dinitrobenzaldehyde, made the condensation with malonic acid extremely slack and it was only after many attempts that the yield of 50% of the theoretical was obtained. It is possible that two nitro-groups in different positions from the above might have behaved differently.

In Part XIII,² it has been shown that the influence of a chloro- or a bromo-group present on the aromatic ring of the aldehyde affected the reaction very favourably, as regards both the speed and the final yield, which includes its purity also. In Part I³ it was shown that salicylaldehyde gave about 51% yield only with a small trace of pyridine: the question may be asked, if a chloro- or a bromo-group were placed on the aromatic ring in salicylaldehyde, would the yield be increased? The investigations described in this paper give data for an answer in the affirmative.

Two bromo-salicylaldehydes have been condensed here with malonic acid, in the presence as well as in the absence of pyridine-traces. Three different products have been obtained from each of the aldehydes, while a fourth was obtained from each by Perkin's method. On the whole the yields in the aldehyde-malonic acid condensations have been much higher than those obtained by Perkin's method, and are also greater than the 51% obtained from the simple salicylaldehyde-malonic acid condensation, though in no case full theoretical yields are obtained as in the condensations with the chloro- and bromo-benzaldehydes.²

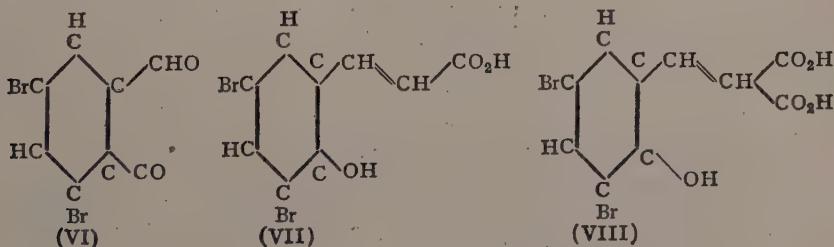


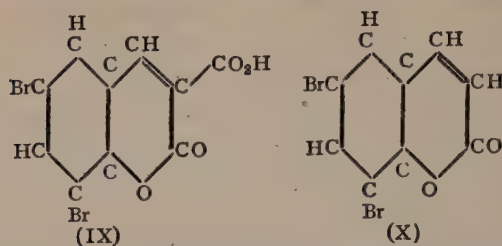


The 5-bromosalicylaldehyde (I) took some time to condense with malonic acid in the presence of pyridine, difficulties being caused by the sublimability of the aldehyde below the water-bath temperature. The sublimated amount was repeatedly scraped off and added to the reacting mass or was washed down with a drop or two more of pyridine. After prolonged heating 5-bromo-orthocoumaric acid (II) was obtained, but the yield was between 50 and 58%. 5-Bromosalicylidene-malonic acid (III) was also formed and was discovered in the filtrate of the bromo-orthocoumaric acid. It was only about 20–25% of the theoretical, but the total yield of the two would be about 78%, which is better than that from the ordinary salicylaldehyde.

As the decarboxylating action of pyridine is well known it was expected that the condensation in the entire absence of pyridine might give more of the dibasic 5-bromosalicylidene-malonic acid (III). However, the main bulk of this condensation was 6-bromo-coumarincarboxylic acid (IV), which melted at 200° and which came out in yields of 92.5%. It was accompanied by another still higher melting product, m.p. 241°, which was too little to be properly investigated. It however melted with effervescence. This was not 6-bromocoumarin (V), which was obtained by following Perkin's method and which melted at 164°.

Condensations with the 3:5-dibromosalicylaldehyde (VI) were a little less difficult, as the sublimation was much less and could be controlled more easily. Perkin's method gave the expected 6:8-dibromocoumarin (X), m.p. 176°. When pyridine was present three products were obtained, two of which were the expected 3:5-dibromo-orthocoumaric acid (VII) and the 3:5-dibromosalicylidene-malonic acid (VIII), melting at 187–189° and 158°, or





157–159°, respectively. These have been identified, but the third, melting at 327° or above, was all used up in purification and qualitative tests. It did not appear to have either a hydroxy or an aldehyde or a carboxylic group and had to be left over for the time. Condensation in the absence of pyridine gave as before 6:8-dibromocoumarincarboxylic acid (IX), in yields of about 74%.

Experimental

*Preparation of 5-Bromosalicylaldehyde.*⁴—5 Grams salicylaldehyde were dissolved in 9.6 c.c. (10 g.) of glacial acetic acid. The flask was placed in freezing-mixture and a solution of bromine 1.8 c.c. (6.6 g.) in glacial acetic acid was added drop by drop with constant stirring. The 5-bromosalicylaldehyde was at once precipitated and washed and dried. The weight of the crude product on drying was 6.5 g., i.e., 82.5% of theory. Recrystallised from dilute alcohol, it melted at 105° (the expected m.p. was 104–105°).

*Condensation by Perkin's method: the Preparation of 6-Bromocoumarin.*⁵—2 G. 5-bromosalicylaldehyde, 4 g. freshly fused sodium acetate and 6 c.c. acetic anhydride were mixed and heated in a flask for five hours at 180–190°. It set to a solid mass at the end of 4.5 hours. The mass was repeatedly extracted with hot water until it gave no colour with ferric chloride. It was then repeatedly washed with ether until that also ceased giving colour with ferric chloride. The white mass left behind melted at 155–165°. It was dissolved in hot caustic soda and reprecipitated by dilute hydrochloric acid. Recrystallised from absolute ethyl alcohol it melted at 164°. (160°, Simonis⁴). The yield was 1 g. or 50%.

Condensation with Malonic Acid with a Trace of Pyridine.—5-Bromosalicylaldehyde 3 g., malonic acid 2.1 g. and 8 drops of pyridine were heated on an oil-bath at 95° for two hours and then at 100–105° for nearly 18 hours. About 8 drops more of pyridine had to be added during the course of this heating. There was much effervescence and the mixture liquefied in the first hour. The sublimed aldehyde was frequently scraped and thrown back into the flask or returned to the mixture by a drop or so of pyridine. After two hours the liquid became quite clear, effervescence had stopped and the

temperature was raised to 100–105°. Gradually the clear liquid became viscous and then set to a solid. The flask was cooled overnight and the contents were extracted with sodium bicarbonate (10%) solution. On acidifying the extract a white precipitate was obtained, which was filtered and washed with water. It melted at 145–148°. Crystallised from ethyl acetate and benzene, it melted at 150–152°. The yield was 50–55%.

It melted without effervescence, gave no colour with ferric chloride but decolorised Baeyer's reagent. Bromine found 32·5%, *bromo-orthocoumaric acid* $C_9H_7O_3Br$ requires 32·9%.

The filtrate was concentrated and on cooling deposited crystals which were removed and the mother-liquor on shaking up with ether and distilling off the ether gave more crystals. These melted at 170°, and on recrystallisation from ethyl acetate and benzene it melted at 175°. It melted with effervescence, gave no colour with ferric chloride and decolourised Baeyer's reagent immediately. A small portion of it was kept in an oil-bath at 180°: it melted and the effervescence continued for some time. After about 15 minutes it was taken out and, on cooling and reheating, melted at 148–150°. When mixed with the bromo-orthocoumaric acid, m.p. 150–152°, the melting-point did not change at all. Bromine found 27·57, 27·58%; *5-bromosalicylidenemalonic acid* $C_{10}H_7O_5Br$ requires 27·87%. Equivalent weight, found by titration with potassium hydroxide, 148·3; required = 143·5. The yield was about 24%, the total yield being about 78%.

Condensation without any Reagent: *6-Bromo-Coumarincarboxylic Acid* (IV)—3 G. 5-bromosalicylaldehyde and 2·1 g. malonic acid were mixed up and heated on the water-bath for 9 hours and then for 8 hours on an oil-bath at 100–105°. The sublimed aldehyde was scraped and added on from time to time. There was plenty of effervescence and after about two hours an opalescent liquid was formed. The mixture never became a clear transparent liquid. One hour after it had solidified again, the temperature was raised up by a change of the bath. The product at the end was extracted with ether to remove the unreacted aldehyde. A grey solid remained undissolved which was filtered off. In the crude condition it melted at 195–200° and weighed 3·7 g. Recrystallised from hot benzene, the melting-point rose only slightly to 200°. It was soluble in hot water and acetone as well, and insoluble in ether.

This experiment was repeated several times, and it was found that only six hours' heating on a water-bath was sufficient to give the same yield, i.e., 92·5%, of the first solid, m.p. 200°, which was the *6-bromocoumarincarboxylic acid*: Bromine, found = 29·43, 29·44%, the acid $C_{10}H_5O_4Br$ requires 29·74%. It melted without effervescence and gave no colour with ferric chloride. It decolourised alkaline permanganate.

When the ethereal extract was treated with sodium dicarbonate solution, it gave much effervescence: excess was then added and the two layers separated. On acidification, the lower layer gave a solid white substance, m.p. 237° (dec.) (y. = 0.3 g.).

This high-melting substance melted at 241° on further purification, but melted with effervescence. It was not in sufficient amount for a clear identification.

3-5-Dibromosalicylaldehyde.⁶—5 g. salicylaldehyde were taken in a flask and to this were added 17.5 g. of bromine (a little more than 2 mol. proportion) drop by drop and with vigorous shaking. The flask was kept at room temperature for two days with occasional shakes: on the third day the whole mass had set to a solid and was taken out with about 500 c.c. or more of water. This was washed free of the excess of bromine. Recrystallised from dilute alcohol it melted at $82-84^{\circ}$ (m.p. 83°)⁶. Yield about 87% of the theoretical.

Condensation by Perkin's method: **6-8-Dibromocoumarin.**⁷—1.4 G. dibromosalicylaldehyde, 2 g. fused sodium acetate and 3 g. acetic anhydride were mixed and heated in the usual way, $170-180^{\circ}$, when the whole mass solidified at the end of three hours. The cold mass was washed with plenty of water, the residue was dried and washed with ether repeatedly till the washing gave no colour with ferric chloride. The residue was dried and recrystallised from rectified spirit. It melted at 176° . Yield about 33%. (6:8-Dibromocoumarin melts at $174-176^{\circ}$).⁷

Condensation in the Presence of Pyridine: **3:5-Dibromo-salicylidenemalonic Acid and 3:5-Dibromo-orthocoumaric Acid.**—Very many condensations had to be tried to get conditions of good yield, as three different substances were found to occur in the product of this single reaction. Higher temperatures than 100° gave better yields of a substance which seemed to melt at about 300° , but has not been identified. Two other products 3:5-dibromosalicylidenemalonic acid (VIII) and 3:5-dibromo-orthocoumaric acid (VII) were also formed, but the amounts of their yields varied greatly with the temperature and the manner of heating. On the other hand ordinary water-bath heating for several hours even gave poor yields and much of the original aldehyde was found remaining unaffected but mixed up with resin.

2.8 G. dibromosalicylaldehyde, 1.4 g. malonic acid and 6 to 8 drops of pyridine were mixed in a flask and the whole was heated on an oil-bath at 110° for 4 hours. There was much effervescence and the mixture changed into a thick viscous mass, a little aldehyde that had sublimed was washed in with a drop or two of pyridine. The temperature was gradually raised to 125° ,

and then the whole was left to itself overnight. The next day the temperature was raised up to 135°, and after one hour quickly to 160°. A solid mixed with much viscous matter appeared to have been formed and the heating was stopped. To the cold flask ether was added when much dissolved, leaving behind a solid which in the crude condition melted at 260°–270°. It was found insoluble in most of the usual organic solvents. Pyridine however dissolved it readily but gave crystals that were very impure and sticky. After a recrystallisation from pyridine-benzene, the substance was washed with dilute hydrochloric acid which removed some of its colour. The substance was then washed with alcohol, then with alcohol plus hydrochloric acid and finally with water to remove the acid. It was finally washed with alcohol and ether. It was now white in colour, and on heating began to get black at 290° and decomposed finally with effervescence at 295–300°. It was again treated with pyridine and benzene, and a little alcohol was added: after two days clear white crystals came out which on drying melted at 323–327°, becoming dark at 310°. It was insoluble in sodium bicarbonate solution and gave no effervescence with it. In fact it gave no indications of the presence of a hydroxy or an aldehyde or a carboxyl group, though it showed bromine.

From the ether-extract the two acids were separated. Addition of sodium bicarbonate solution to it gave effervescence, so excess was added and it was allowed to remain for a couple of hours when white crystals of a sodium salt came out. These were filtered off, treated with hydrochloric acid and with water. The solid obtained after recrystallisation melted at 185–187° without effervescence. This was *dibromo-orthocoumaric acid*, soluble in ether, alcohol, etc., but insoluble in benzene (hot or cold). Found Bromine = 49·38%, the acid $C_9H_6O_3Br_2$ requires 49·68%. The best yield = 31%.

The filtrate contained the soluble sodium salt of the dibromosalicylicidenemalonic acid, which was decomposed by dilute hydrochloric acid. It melted with effervescence at 140–150°, but on recrystallisation from alcohol, it melted at 157–159°. Heated alone on a naked flame for some time it gave off carbon dioxide and was changed into the monobasic acid, m.p. 187–189°. Heating with pyridine also brought about the same change. Found Bromine = 43·28%, the acid $C_{10}H_6O_5Br_2$ requires 43·71%. The best yield = 22%.

Condensation in the Absence of any Condensing Reagent: 3:5-4:6-Dibromo-coumarincarboxylic Acid (IX).—3:5-Dibromosalicylaldehyde 1·4 g. and malonic acid 0·7 g. were mixed and heated together for 5 hours on a water-bath and then for one hour in an oil-bath at 130°. In another experiment the heating was at 130° at the beginning but was then lowered to 110–120° after the whole mass had melted, the total amount being six hours. The

product in both cases was the same and the yield also was the same about 76%. The product was extracted with ether, when the dibromocoumarin-carboxylic acid was left undissolved. It was recrystallised from alcohol and melted at 224–226°. The ethereal extract was a mixture of the same acid with some of the unreacted aldehyde. Found Bromine = 45.72%, the acid $C_{10}H_4O_4Br_2$ requires 45.97%. It appeared to be dimorphous; crystallised from alcohol, it came out in white needles, and from benzene it came out in cubes.

Acknowledgements are due to Mr. Mahendra Rai Kikani for a few preliminary experiments on this subject.

Summary

5-Bromosalicylaldehyde and 3:5-dibromosalicylaldehyde have both been condensed with malonic acid in the presence of pyridine as well as in its entire absence, and the yields are on the whole greater than were obtained from the condensation of salicylaldehyde with malonic acid in the presence of pyridine, the highest being 92.5%. Perkin's reaction gave different products altogether and in much smaller yields.

REFERENCES

1. Pandya, Ittyerah, and Miss Pandya *J. Uni. Bom.*, 1941, **10**, Part 3, 78.
2. Pandya and Miss Pandya .. *Proc. Ind. Acad. Sci., A*, 1941, **13**, 112.
3. Kurien, Pandya and Surange *J. I. C. S.*, 1934, **11**, 823.
4. Piria .. *Annal.*, **30**, 171 ; Auwers and Bürger, *Ber.*, 1904, **37**, 3934.
5. Perkin .. *J. C. S.*, **24**, 41 ; Simonis and Wenzel, *Ber.*, **33**, 1962 and 2327.
6. Loewig .. *Berzelius' Jahresberichte*, **20**, 313.
7. Perkin .. *J. C. S.*, **24**, 42 ; Simonis and Wenzel, *Ber.*, **33**, 1964.

COLORIMETRIC ESTIMATION OF BORIC ACID WITH PENTAMETHYLQUERCETIN

BY K. NEELAKANTAM AND S. RANGASWAMI

*(From the Departments of Chemistry and Chemical Technology,
Andhra University, Waltair, now at Guntur)*

Received April 15, 1943

SEVERAL methods for the determination of boric acid are known and of these the alkalimetric method which is largely employed depends on the titration of boric acid with standard alkali in the presence of glycerol, mannitol or invert sugar. Gravimetric methods depending on the absorption of boric acid in a suitable reagent and determining the increase in weight are also known.¹ Both types of methods yield satisfactory results only with appreciable amounts of boric acid. Colorimetric methods which have been suggested in the literature for the estimation of small amounts of boron depend on the reaction of boric acid with (a) turmeric, (b) curcumin in presence of oxalic acid, and (c) quinalizarin dissolved in sulphuric acid. To these may be added the unusual colorimetric procedure of Stahl² which depends on the comparison of the intensities of the green flame colour given by methyl borate from the test and standard samples.

Hebebrand³ showed that 0.1 mg. of boric acid gives a feeble brown tint whilst 10.0 mg. of the acid gives a bright rose-red colour with a 1% solution of turmeric and a colorimetric method was developed on this basis. The colouration is somewhat fugitive, and is destroyed by prolonged exposure to light and also by boiling. Bertrand and Agulhon⁴ employing strips of turmeric paper carried out successfully the estimation of 0.1 to 0.0001 mg. of boric acid. This method depends on the comparison of the lengths of the colourations produced on the turmeric strips with the test and standard solutions of boric acid in presence of dilute hydrochloric acid. Schäfer⁵ pointed out that concentrated hydrochloric acid itself gives a red colour with turmeric and this changes progressively to yellow on dilution with water. Hence the concentration of hydrochloric acid employed is of importance in this method.

The second colorimetric method depends on the red colour given by boric acid with curcumin in presence of oxalic acid. Using this method as much as 2.0 mg. of boron trioxide can be estimated (Snell⁶). Neither of the above two methods, however, is rapid.

The third colorimetric method depends on the quinalizarin-boric acid reaction in presence of concentrated sulphuric acid. The solution of the reagent in concentrated sulphuric acid is itself violet in colour and this changes to blue with increasing additions of boric acid, the actual colour produced being composed of varying amounts of red and blue. Scharrer and Gottschall⁷ employed the method for the estimation of 120 to 12 γ of boric acid. Smith⁸ found that it was necessary to work with concentrations of boric acid less than 0.04 mg. per c.c. and that the lower limit was 0.002 mg. per c.c.

Using the photo-electric colorimeter Olson and De Turk⁹ estimated amounts up to 0.03 mg. of boron. These authors found that maintenance of constant temperature during the estimation was important for obtaining good duplicates and that decrease in the concentration of the sulphuric acid decreased the sensitivity, so that a definite high concentration of acid had to be employed. Patricia W. Mansell¹⁰ using the Lovibond tintometer found that about 2 γ of boron was the most satisfactory quantity to measure. It is evident from the above that this method is available only for the estimation of very small quantities of boric acid.

Stahl (*loc. cit.*) found that quantities of the order of 0.3 mg. or more of boron trioxide in the upper limit and smaller quantities of the order of 0.0022 to 0.007 mg. could be determined with an accuracy of 0 to 15% by his method.

Several other colour reactions for boric acid of great sensitivity have been described in the literature, but no attempt seems to have been made to adapt them for colorimetric work. Rangaswami and Seshadri¹¹ have recently pointed out that the boric acid reaction characteristic of 5-hydroxy- and 5-methoxyflavones and -flavonols and 2-hydroxy- and 2-methoxy-chalkones first described by Wilson¹² and subsequently developed by them is capable of application for the detection of boric acid itself. These compounds in anhydrous acetone solution containing anhydrous citric acid undergo a change of colour on the addition of traces of boric acid. Compounds that are themselves coloured yellow become deeper yellow on the addition of boric acid while those that give only colourless solutions in acetone containing citric acid develop a yellow colour on the addition of boric acid. Using pentamethylquercetin, which gives a practically colourless solution in acetone containing citric acid only, as the reagent (Rangaswami and Seshadri, *loc. cit.*) showed that 1 part of boric acid in 30,000 parts of solution could be easily detected—a reaction of a fairly high degree of sensitivity. This reaction has now been investigated in detail with a view to develop a method for the colorimetric estimation of boric acid.

Experimental

Solutions:

(1) *Reagent*.—Dry pentamethylquercetin (225 mg.) was dissolved in anhydrous acetone and the solution made up to 100 c.c. with same solvent. For this purpose acetone (extra pure) was dehydrated by standing over fused calcium chloride for 72 hours and then distilled under anhydrous conditions.

(2) *Boric Acid*.—A pure sample of boric acid was finely powdered and dried in a steam oven for 6 hours. 200 mg. of the acid was accurately weighed out, dissolved in anhydrous acetone and the solution made up to 100 c.c. with the same solvent. 5 c.c. of this solution was diluted to 25 c.c. with the same solvent and used as the standard.

(3) *Citric Acid*.—Citric acid (pure) crystals were finely powdered and dehydrated by drying in a steam oven for 30 hours. 50 g. of the acid were dissolved in 500 c.c. of anhydrous acetone and the solution was filtered rapidly through a plug of cotton wool, to remove some finely divided insoluble material.

In preparing the above solutions carefully dried apparatus was used and the solutions were kept in well-stoppered dry bottles.

(4) *Potassium chromate*.—1.0 g. of potassium chromate (A.R) was weighed accurately, dissolved in water and the solution made up to 100 c.c. with water. 20 c.c. of the solution was pipetted out and diluted to 100 c.c. with water. The latter solution was employed in the experiments.

Preliminary Investigation

The colour (yellow) was developed by adding to a measured volume of the boric acid solution an excess of the reagent solution—more than one molecular proportion—and then diluting to volume with the 10% citric acid solution.

As the various aspects of this colour reaction had not been studied before, they were investigated now and the results are reported below :—

1. No colour was developed until the citric acid solution was added.
2. The yellow colour developed was progressively reduced in intensity and it finally disappeared altogether on dilution with anhydrous acetone free from citric acid. Experiments showed that this could not be a mere dilution effect.
3. Attempts to use the Lovibond tintometer for the measurement of colour and investigation of its variation, if any, with time were not successful on account of the volatility of the solvent at the temperatures obtaining in the

tintometer and also due to the rapid absorption of moisture of the citric acid solution.

4. Experiments carried out with the Duboscq type of colorimeter (balancing method) gave satisfactory results with identical solutions. With solutions which differed slightly in concentration of boric acid, however, erratic results were obtained showing thereby that Beer's Law does not hold good.

5. The intensity of colour in a given case depended on the actual amount of reagent solution added and possibly also on the amount of citric acid solution employed so that for good reproducibility definite conditions had to be prescribed.

6. The duplication method was more successful than the balancing method but here again the same factors as in (3) above precluded satisfactory results. Consequently it was necessary to work with closed vessels and with the minimum of exposure to air.

7. With quantities of boric acid less than 0.4 mg. the yellow colour developed was considerably reduced in intensity on dilution to 25 c.c. with the citric acid solution. Experiments showed that the magnitude of this reduction was quite out of proportion to what may be expected on the basis of dilution. With 0.4 mg. and above of boric acid apparently this did not occur. From this it appears that different final dilutions must be adopted depending on the amount of boric acid present in the test.

8. The yellow colours obtained resembled closely, though not perfectly, the pure yellow of potassium chromate solutions so that the former could be matched with the latter. In this manner permanent standards for use in routine work could be easily prepared.

Based on the above results the following empirical method has been worked out for the approximate estimation of small quantities of boric acid ranging from 0.4 to 1.8 mg.

Procedure

An aliquot part of the standard boric acid solution was pipetted out into a dry 50 c.c. Nessler cylinder having a graduation at 25 c.c., 5 c.c. of the reagent solution added and the volume made up to the 25 c.c. mark with the citric acid solution. After stirring, the cylinder was tightly corked. 15-20 c.c. of water were placed in another cylinder of the same dimensions and the matching was carried out by adding the standard chromate solution from the burette in the usual manner for the duplication method. Except during actual matching the cylinder containing the test solution was kept corked. The matching was repeated three or four times in each case. With quantities of

boric acid of the order of 1.2 mg. and above, the intensities of the yellow colour, when the whole of the solution (25 c.c.) was employed, were felt to be too deep for satisfactory matching. In these cases, therefore, after making up to 25 c.c. with the citric acid solution, the volume was halved using a measuring cylinder and the matching carried out. The total intensity (for 25 c.c.) was obtained in terms of the chromate solution by doubling the value obtained.

Results

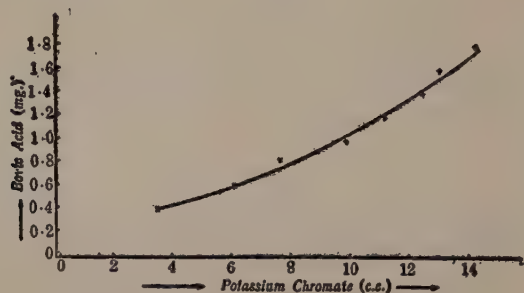
The results obtained are recorded in Table I. The amounts of boric acid were plotted against the mean volumes of the chromate solution and a mean curve was drawn (*cf.* Graph). To evaluate the magnitude of the

TABLE I

Boric acid mg.	Potassium chromate c.c.	Mean volume c.c.	Pot. chromate c.c. (interpolated)	Deviation %
1	2	3	4	5
0.4	3.2 3.3 3.7	3.4	3.4	nil
0.6	6.1 5.9 6.3	6.1	6.1	nil
0.8	7.9 7.4 7.6	7.6	8.0	-5.0
1.0	9.8 9.8 9.9	9.8	9.5	+3.2
1.2*	11.0 11.4 10.9	11.1	10.8	+2.8
1.4*	11.8 12.4 12.6	12.3	12.1	+1.7
1.6*	13.2 12.4 13.2	12.9	13.2	-2.3
1.8*	14.0 14.0 14.4	14.1	14.3	-1.4

* After developing colour only half the test solution was employed for matching.

errors in matching, the mean volumes of the chromate solution corresponding to the boric acid taken were obtained by interpolation on the graph



and are recorded in column 4. The percentage deviation of the mean volumes (experimental) from the interpolated figures was then calculated and the results are recorded in column 5.

In order to test the relationship thus established, the colour was developed with other known quantities of boric acid and then matched with the chromate solution as before. From the mean volume of the chromate solution required, the amount of boric acid was read out from the graph. The results obtained are given in Table II.

TABLE II

Boric acid taken mg.	Potassium chromate c.c.	Mean volume c.c.	Boric acid found mg.	Error %
1	2	3	4	5
0.48	5.5 5.6 5.7	5.6	0.55	+14.6
0.68	6.5 6.8 6.8	6.7	0.65	- 4.4
1.48*	13.9 13.6 13.9	13.8	1.7	+14.9

* After developing colour only half the test solution was employed for matching.

Discussion

The figures given in Table I, column 2, show a variation of 0.5 c.c. in matching except in two cases where it reaches 0.8 c.c. This increase obviously arises from the fact that the errors in matching are multiplied by two (*vide*

supra) according to the procedure adopted. The maximum deviation from the mean volumes (column 3) is only 0.5 c.c. Thus the figures in column 2 when compared with the mean volumes represent maximum errors in matching of about 15 and 3.5% on the lowest and highest limits of boric acid respectively. However, the deviations of the mean volumes from the mean curve range from 0 to 5.0% (*cf.* columns 4 and 5) so that if the mean volumes are employed for interpolation on the graph the deviation from the truth due to errors in matching does not exceed 5.0%.

The results given in Table II, however, show a maximum error of about 15% in the estimation of boric acid by interpolation of the mean volumes (column 3) on the graph. It appears probable that the higher error is partly due to the difficulty in measuring small volumes of boric acid solution in the highly volatile solvent, acetone. It may, however, be pointed out in this connection that errors as high as 10% are not unusual in visual colorimetric methods.

Regarding the mechanism of the reaction the following may be mentioned:—

In aqueous solutions boric acid reacts with polyhydroxy compounds such as glycerine, mannitol, etc., to form simple esters; with the *o*-hydroxy carbonyl compounds and in presence of the dehydrating agent, sulphuric acid, however, it yields inner complex (chelate) esters. The interaction of boric acid with the O-Hydroxy-carbonyl compounds, *viz.*, 5-hydroxy-flavones and -flavonols and the 2-hydroxy-chalkones, in presence of anhydrous citric acid may perhaps be explained on the assumption that the latter serves as a dehydrant, though the possibility of interaction between the hydroxy acid (citric acid) and boric acid as a preliminary to the former reaction could not be altogether ignored. The mechanism of the interaction of boric acid with the 5-methyl ethers of the above hydroxy-flavones and -flavonols and 2-methyl ethers of the above hydroxy-chalkones is obviously more complicated as no free hydroxyl, ortho to the carbonyl group, is available in any one of these compounds. The part played by the anhydrous citric acid is itself not quite clear and consequently the disappearance of colour on dilution with acetone, free from citric acid, could not be explained. The available evidence is meagre and hence the reaction must be regarded as empirical at present.

Regarding the method itself the following points may be considered:—

1. The use of the highly volatile solvent, acetone is apparently a serious disadvantage but it is of interest to note in this connection that even the more volatile ether is used for the extraction of nickel dimethyl glyoxime complex

in colorimetric work.^{6a} The use of a less volatile solvent is an obvious solution of the difficulty but the choice is limited by the solubilities of the substances involved and also by the fact that hydroxylic solvents could not be employed.

The present method possesses the advantage that the blank is practically colourless whereas in the three colorimetric methods referred to already the blanks are coloured. Its chief advantage, however, is in its rapidity as compared with the turmeric and curcumin methods (*loc. cit.*), although the results obtained are only approximate.

3. The need for the rigorous exclusion of moisture is apparently a serious drawback of the method, but it may be pointed out that the drying of the reagents can be readily accomplished and the time taken in drying the few pieces of apparatus could not be regarded as of serious consequence. Further the need for stoppering the Nessler cylinder containing the test solution except during matching is not a great inconvenience in practice.

Summary

A new method for the approximate colorimetric estimation of boric acid depending on the yellow coloration yielded by boric acid with pentamethyl-quercetin in presence of citric acid in anhydrous acetone medium has been described. The method is empirical in character and gives results with a maximum error of about 15% with quantities of boric acid ranging from 0.4 to 1.8 mg.

The authors wish to express their thanks to Professor T. R. Seshadri for valuable help rendered in the course of this investigation.

REFERENCES

1. Mellor .. *A Treatise on Chemical Analysis*, 1938, 653.
2. Stahl .. *Z. anal. chem.*, 1931, 83, 340 ; cf. *Chem. Abs.*, 1931, 25, 2387.
..... .. *Z. anal. chem.*, 1935, 101, 348 ; cf. *Chem. Abs.*, 1935, 29, 5774.
3. Hebebrand .. *British Chem. Abs.*, 1902, 2, 354.
4. Bertrand and Agulhon .. *Chem. Abs.*, 1914, 8, 884, 1312.
5. Schäfer .. *Z. anal. chem.*, 1937, 110, 11 ; cf. *Chem. Abs.*, 1937, 31, 437.
6. Snell .. *Colorimetric Analysis*, 1936, 1, 526.
- 6a. *Ibid.*, p. 316.
7. Scharrer and Gottschall .. *Brit. Chem. Abs.*, 1935, B, 820.
8. Smith .. *Organic Reagents for Metals*, cf. Hopkin and Williams, Ltd.,
1938, 109.
9. Olson and De Turk .. *Chem. Abs.*, 1941, 35, 1723.
10. Patricia W. Mansell .. *Ibid.*, 1941, 35, 6536.
11. Rangaswami and Seshadri .. *Proc. Ind. Acad. Sci.*, 1942, 16 A, 129.
12. Wilson .. *J. A. C. S.*, 1939, 2303.

A NOTE ON POISSON DISTRIBUTION

BY K. SANKARA PILLAI

(Travancore University)

Received March 23, 1943

(Communicated by Prof. K. B. Madhava, F.A.Sc.)

1. Introduction

POISSON distribution like the binomial, contains only one parameter and is of very wide application in statistical work. The usual estimate for the parameter is the sample arithmetic mean obtained by the method of maximum likelihood. The method of least squares yields in this case an estimate that cannot be expressed as a convenient function of the observed values. A slight modification in the method of approach to the problem of estimation allows a direct application of the least square principle and gives an estimate which is elegant though not as simple as the maximum likelihood estimate. A discussion on the estimate so obtained is given in this paper.

2. Estimate for m

Let the population frequencies be denoted by

$$Y_k = \frac{N \cdot m^k e^{-m}}{\Gamma(k+1)}, \quad (k = 0, 1, 2, \dots) \quad (1)$$

and the observed frequencies by

$$y_k \quad (k = 0, 1, 2, \dots) \quad (2)$$

Also

$$N = y_0 + y_1 + y_2 + \dots + y_n.$$

We have in the population

$$Y_{k+1} = \frac{m}{k+1} \cdot Y_k \quad (3)$$

Since the relation (3) exists in the population, we shall assume that in a sample also an approximately similar relationship holds good. Hence

$$y_{k+1} = \frac{m}{(k+1)} \cdot y_k + \epsilon_k \quad (k = 0, 1, \dots, n-1) \quad (4)$$

where the ϵ 's are small. To estimate m we minimise

$$\sum_0^{n-1} \epsilon_k^2 = \sum_0^{n-1} \left[y_{k+1} - \frac{m}{k+1} \cdot y_k \right]^2$$

By differentiation, we get the required estimate

$$m_2 = \frac{\sum_0^{n-1} [y_k \cdot y_{k+1} / (k+1)]}{\sum_0^{n-1} [y_k^2 / (k+1)^2]} \quad *$$

It may be interesting to note that in the case of the binomial distribution

$$Y_{k+1} = \frac{n-k}{k+1} \cdot \frac{p}{1-p} Y_k.$$

Using the method adopted above the estimate for p is

$$\Sigma \frac{n-k}{k+1} \cdot y_k \cdot y_{k+1} / \left[\Sigma \left(\frac{n-k}{k+1} y_k \right)^2 + \Sigma \frac{n-k}{k+1} \cdot y_k \cdot y_{k+1} \right].$$

The statistics m_2 satisfies the criterion of consistence, for the population value of m_2 is given by

$$\frac{N^2 \cdot e^{-2m} \cdot \sum_0^{n-1} \frac{m^{2k+1}}{\Gamma(k+2) \cdot \Gamma(k+2)}}{N^2 \cdot e^{-2m} \cdot \sum_0^{n-1} \frac{m^{2k}}{\Gamma(k+2) \cdot \Gamma(k+2)}} = m$$

Though the statistic is a consistent one, it is clear that it does not satisfy the criterion of sufficiency.

3. Efficiency of m_2

To determine the efficiency of the estimate m_2 , we proceed to calculate the standard error of m_2 in large samples.

We have

$$m_2 = u/v \text{ where} \quad (6)$$

$$u = \sum_0^{\infty} y_k \cdot y_{k+1} / (k+1); \quad v = \sum_0^{\infty} y_k^2 / (k+1)^2$$

Also let

$$U = \sum_0^{\infty} Y_k \cdot Y_{k+1} / (k+1); \quad V = \sum_0^{\infty} Y_k^2 / (k+1)^2 \quad (7)$$

In repeated samples, let us denote the small variation in the class frequency y_k by δy_k ($k=0, 1, 2, \dots$) and the corresponding variations in u , v , m_2 , by δu , δv and δm_2 respectively. Hence

$$\begin{aligned} y_k &= Y_k + \delta y_k \quad (k=0, 1, \dots, \infty) \\ u &= U + \delta u, \quad v = V + \delta v, \quad m_2 = m + \delta m_2. \end{aligned} \quad \dagger \quad (8)$$

* We shall assume that m_1 denotes the max. likelihood estimate, viz.,

$$m_1 = (y_0 + y_1 + \dots + y_n) / n$$

† We assume $y_k = 0$ ($k = n+1, n+2, \dots$).

From (6) and (8) we have

$$V \cdot \delta m_2 = \delta u - m_2 \cdot \delta v. \quad (9)$$

Further,

$$\delta u = \sum_0^{\infty} [Y_k \cdot \delta y_{k+1} + Y_{k+1} \cdot \delta y_k] \div (k+1). \quad (10)$$

$$\delta v = \sum_0^{\infty} [2Y_k \cdot \delta y_k] \div (k+1)^2. \quad (11)$$

Using (10), (11) and (3) in (9), we have,

$$V \cdot \delta m_2 = \sum_1^{\infty} \left[\frac{Y_{k-1}}{k} - \frac{Y_{k+1}}{k+1} \right] \cdot \delta y_k - Y_1 \cdot \delta y_0. \quad (12)$$

Let

$$P_k = \frac{Y_{k-1}}{k} - \frac{Y_{k+1}}{k+1} \quad (13)$$

Equation (12) can now be written as

$$V \cdot \delta m_2 = \sum_1^{\infty} P_k \cdot \delta y_k - Y_1 \cdot \delta y_0. \quad (14)$$

Squaring (14) and taking expectations,

$$\begin{aligned} V^2 \cdot E(\delta m_2^2) &= \sum_1^{\infty} P_k^2 \cdot E(\delta y_k^2) + Y_1^2 \cdot E(\delta y_0^2) \\ &\quad - 2Y_1 \cdot \sum_1^{\infty} P_k \cdot E(\delta y_0 \cdot \delta y_k) + \sum_{k \neq j}^{\infty} \sum_1^{\infty} P_k \cdot P_j \cdot E(\delta y_k \cdot \delta y_j) \end{aligned} \quad (15)$$

Since

$$E(\delta y_k^2) = Y_k \cdot (1 - Y_k/N) \text{ and}$$

$$E(\delta y_k \cdot \delta y_j) = -Y_k \cdot Y_j/N \quad (k \neq j)$$

Equation (15) becomes,

$$\begin{aligned} V^2 \cdot \sigma_2^2 &= \sum_1^{\infty} P_k^2 \cdot Y_k + Y_1^2 \cdot Y_0 \\ &\quad - \frac{1}{N} \left[\sum_1^{\infty} P_k^2 \cdot Y_k^2 + \sum_{k \neq j}^{\infty} \sum_1^{\infty} P_k \cdot P_j \cdot Y_k Y_j - 2Y_0 \cdot Y_1 \sum_1^{\infty} P_k Y_k + Y_0^2 \cdot Y_1^2 \right] \\ &= \sum_1^{\infty} P_k^2 \cdot Y_k + Y_1^2 \cdot Y_0. \end{aligned} \quad (16)$$

Substituting the value of P_k , we get after reduction,

$$\sigma_2^2 = \frac{e^m}{N} \frac{\sum_1^{\infty} \frac{m^{3k-1}}{k(k!)^3} - 2 \sum_1^{\infty} \frac{m^{3k}}{k! (k+1)^2} + \sum_1^{\infty} \frac{m^{3k-2}}{(k!)^3}}{\left[\sum \frac{m^{2k}}{(k+1)^2} \right]} \quad (17)$$

* We assume that σ_1 and σ_2 are the standard errors of m_1 and m_2 respectively.

It has not been possible to obtain σ_2 in terms of elementary functions. The denominator can be expressed in terms of known series, it being equal to

$$[I_0(2m) - 1]^2 m^4$$

where $I_0(2m)$ is the Bessel Function of order zero with a purely imaginary argument. However the other series are rapidly converging and for particular values of m the sum may be calculated to any degree of accuracy.

The standard error of m_2 , makes it possible to calculate the efficiency E of m_2 , the standard error of the maximum likelihood estimate being equal to m/N

$$E = \sigma_1^2 / \sigma_2^2. \quad (18)$$

For small values of m Table I below gives E . For large values of m the numerical calculation is heavy and hence we proceed to find an asymptotic formula for E .

The asymptotic expansions for the several series in equation (17) are as follows:—

$$I_0(2m) \sim \frac{e^{2m} [1 + 0(1/m)]}{2 \cdot \sqrt{m\pi}} \quad (19)$$

$$\sum_1^\infty \frac{m^{2k-1}}{k \cdot (k!)^3} \sim e^{2m} \left[1 + \frac{7}{9m} + 0(1/m^2) \right] \div (2\pi \cdot \sqrt{3} \cdot m^3) \quad (20)$$

$$\sum_1^\infty \frac{m^{3k}}{[k \cdot (k+1)]^2} \sim \frac{e^{3m} [1 - 2/9m + 0(1/m^2)]}{2\pi \sqrt{3} m^3} \quad (21)$$

$$\sum_1^\infty \frac{m^{2k-2}}{(k!)^2} \sim \frac{e^{3m} [1 + 1/9m + 0(1/m^2)]}{2\pi \cdot m^3 \cdot \sqrt{3}} \quad (22)$$

Using these expansions, we get

$$E = 3 \cdot \sqrt{3}/8 = 0.6495.$$

TABLE I
Efficiency of m_2

m	0	.5	1	1.5	2	3	4	5	10	∞
E	1	.4929	.3617	.3182	.3542	.4481	.5215	.5583	.5910	.6495

4. Numerical Illustration

In the example given below both m_1 and m_2 are calculated and the corresponding values of the frequencies tabled and compared.†

† See *Asymptotic Developments of Functions defined by Series*, Walter B. Ford, p. 85. For (20), (21) and (22) see appendix.

‡ The example is taken from *The Theory of Probability*, Jeffries, p. 59.

TABLE II

The Frequency of Nuclei of Condensation in Aitken Dust Counter

Number	0	1	2	3	4	5	6	7	8
Observed Frequency	23	56	88	95	73	40	17	5	3
Calculated Frequency—												
1. $m_1 (=2.93)$	25	65	88	82	61	38	21	10	4
2. $m_2 (=2.99)$	20	60	90	90	67	40	20	9	3
Deviations—												
1. Based on m_1	-2	-9	..	13	12	2	-4	-5	-1
2. Based on m_2	3	-4	-2	5	6	0	-3	-4	0

Root mean square when m_1 is the estimate = 7.0do. m_2 do. = 3.6.

5. Conclusion

The object of this paper has been to get an estimate for the parameter in the Poisson distribution, based on the method of least squares. The statistic obtained is found to satisfy the condition of consistence; it is, however, not a sufficient statistic. Its standard error has been found and its efficiency determined, and an asymptotic value for the latter obtained.

In conclusion, the author wishes to thank Dr. U. Sivaraman Nair for his kind help in the preparation of this paper. The author is also grateful to the University of Travancore for allowing him to carry on this work.

6. Mathematical Appendix

In what follows we shall prove a theorem pertaining to the asymptotic development of the function $F(z)$ defined by the series,

$$F(z) = \sum_0^{\infty} \frac{h(n) \cdot z^{3n}}{\Gamma(n+a_1) \cdot \Gamma(n+a_2) \cdot \Gamma(n+a_3)}.$$

The asymptotic expansion is based on the three Theorems given below§:

Theorem I. If the co-efficient $g(n)$ of the power series

$$f(z) = \sum_0^{\infty} g(n) \cdot z^n; \text{ radius of convergence } > 0 \quad (1)$$

may be considered as a function $g(w)$ of the complex variable $w = x + iy$ and as such satisfies the two following conditions when considered throughout any arbitrary right half plane $x > x_0$:

§ See *Asymptotic Developments*, Ford, pp. 4, 30.

(a) is single valued and analytic,

(b) is such that for all $|y|$ sufficiently large one may write

$$|g(x+iy)| < K \cdot e^{\epsilon|y|} \quad (2)$$

where ϵ is an arbitrarily small positive quantity given in advance and where K depends only upon x_0 and ϵ , then the function $f(z)$ defined by (1) is analytic throughout any sector S (vertex at the origin) of the z -plane which does not include the positive half of the real axis and $f(z)$ within S is developable asymptotically as follows:—

$$f(z) \sim -\sum_1^{\infty} g(-n)/z^n \quad (3)$$

Theorem II. If condition (b) stated in Theorem I is changed to (c) $g(w)$ is such that for all $|y|$ sufficiently large one may write

$$|g(x+iy)| < K \cdot e^{(\pi+\epsilon)|y|}$$

other condition remaining the same, then the function $f(z)$ defined in (1), when considered throughout any sector S (vertex at the origin) of the z -plane which does not contain the negative half of the real axis, may be expressed in the form

$$f(z) = \int_{-l-\frac{1}{2}}^{\infty} g(x) \cdot z^x dx - \sum_1^l \frac{g(-n)}{z^n} + \xi_l(z) \quad (5)$$

in which l is any positive integer ≥ 1 and

$$\lim_{z \rightarrow \infty} z^l \xi_l(z) = 0.$$

Theorem III. Let $P(w)$ be a function of the complex variable $w = x+iy$, which is single valued and analytic throughout the half plane $x > x_0$, where x_0 has some negative value previously assigned; also suppose that as $w \rightarrow \infty$ along any ray emanating from the origin upon which $-\pi/2 < \arg w < \pi/2$, the same function satisfies the following condition, in which c is a constant whose value is independent of the ray selected,

$$\lim_{w \rightarrow \infty} P(w) = c$$

then, as $z \rightarrow \infty$ along any ray emanating from the origin in the z -plane upon which $-\pi/2 < \arg z < \pi/2$, we shall have,

$$\lim_{z \rightarrow \infty} e^{-z} \cdot \int_0^{\infty} \frac{P(x) \cdot z^{x-1}}{\Gamma(x)} dx = c \quad (6)$$

where the integration is understood to be along the real axis.

Using these three theorems we proceed to prove:—

Theorem IV. Let $F(z)$ be a function of the complex variable z defined by the series

$$F(z) = \sum_0^{\infty} \frac{h(n)}{\Gamma(n+a_1) \cdot \Gamma(n+a_2) \cdot \Gamma(n+a_3)} \cdot z^{3n} \quad (7)$$

in which a_1, a_2, a_3 are constants and in which $h(n)$ may be regarded as a function $h(w)$ of the complex variable $w = x + iy$ and as such satisfies the two following conditions:—

(a) $h(w)/\Gamma(w+a_1) \cdot \Gamma(w+a_2) \cdot \Gamma(w+a_3)$ is a single valued, analytic function of w throughout the finite w -plane,

(b). $h(w)$ is such that, when considered for values of w of large modulus lying in the right half plane $R(w) = x > x_0$ where x_0 is some assignable number, it may be expressed in the form

$$h(w) = \sum_{i=0}^{s+1} \frac{b_i \cdot \Gamma(w+k)}{\Gamma(w+k+i)} + \frac{\delta(w, s) \cdot \Gamma(w+k)}{\Gamma(w+k+s+1)} \quad (8)$$

in which the b_i 's are constants and $\lim_{w \rightarrow \infty} \delta(w, s) = 0$ ($s = 0, 1$).

Then $F(z)$ has the following asymptotic development

$$F(z) \sim \frac{e^{3z}}{2\pi \cdot \sqrt{3} \cdot z^p} \left[\sum_0^{\infty} \frac{C_m}{(3z)^m} \right], \quad -\pi/6 < \arg z < \pi/6$$

(9)

where $p = a_1 + a_2 + a_3 - 2$.

*Proof.** Let $f(z)$ be the function defined by the series

$$f(z) = \sum_0^{\infty} g(n) \cdot z^n, \quad (10)$$

where
$$g(n) = \frac{h(n/3)}{\Gamma(n/3+a_1) \cdot \Gamma(n/3+a_2) \cdot \Gamma(n/3+a_3)}. \quad (11)$$

We have

$$F(z) = \frac{1}{2} [f(z) + f(z \cdot e^{2\pi i/3}) + f(z \cdot e^{-2\pi i/3})] \quad (12)$$

so that our problem reduces to that of obtaining asymptotic expansions for the series occurring in (12).

$g(n)$ satisfies the conditions given in Theorem I and hence for all z of large modulus lying upon any ray for which $\pi/2 < \arg z < 3\pi/2$,

$$f(z) \sim - \sum_{.1}^{\infty} \frac{h(-n/3)}{\Gamma(-n/3+a_1) \cdot \Gamma(-n/3+a_2) \cdot \Gamma(-n/3+a_3)} \cdot z^n \quad (13)$$

* The method of proof closely follows that adopted by Walter B. Ford in *Asymptotic Developments*, pp. 73.

$g(n)$ also satisfies the condition given in Theorem II and hence for all z of large modulus lying on any ray for which $-\pi < \arg z < \pi$,

$$f(z) = Q(z, l) - \sum_{n=1}^l \frac{h(-n/3)}{\Gamma(-n/3+a_1) \cdot \Gamma(-n/3+a_2) \cdot \Gamma(-n/3+a_3)} \cdot z^n + \epsilon_1(z) \quad (14)$$

where

$$Q(z, l) = \int_{-l-\frac{1}{2}}^{\infty} \frac{h(x/3) \cdot z^x}{\Gamma(x/3+a_1) \cdot \Gamma(x/3+a_2) \cdot \Gamma(x/3+a_3)} dx \quad (15)$$

and $\lim_{z \rightarrow \infty} z^l \cdot \epsilon_1(z) = 0$

l being any arbitrarily large positive integer.

In order to study the behaviour of $Q(z, l)$ when z is large let us put

$$p = a_1 + a_2 + a_3 - 2 \quad (16)$$

and then write (15) in the form

$$Q(z, l) = \int_{-l-\frac{1}{2}}^{\infty} \frac{\Gamma(x+p+1) \cdot h(x/3)}{\Gamma(x/3+a_1) \cdot \Gamma(x/3+a_2) \cdot \Gamma(x/3+a_3)} \cdot \frac{z^x dx}{\Gamma(x+p+1)} \quad (17)$$

Let us change the variable from x to t by the transformation $x+p=t$. Then we have

$$Q(z, l) = \int_{p-l-\frac{1}{2}}^{\infty} \frac{\Gamma(t+1) \cdot h\left(\frac{t-p}{3}\right)}{\Gamma\left(\frac{t-p}{3}+a_1\right) \cdot \Gamma\left(\frac{t-p}{3}+a_2\right) \cdot \Gamma\left(\frac{t-p}{3}+a_3\right)} \cdot \frac{z^{t-p} dt}{\Gamma(t+1)} \quad (18)$$

in which the path of integration extends from the point $t=p-l-1/2$ to infinity in the direction of the positive real axis of t .

Now,

$$\Gamma(t+1) = \frac{3^{t+1/2}}{2\pi} \Gamma(t/3+1/3) \cdot \Gamma(t/3+2/3) \cdot \Gamma(t/3+1).$$

Using this result in (18)

$$Q(z, l) = \frac{\sqrt{3}}{2\pi z^p} \int_{p-l-\frac{1}{2}}^{\infty} \frac{H(t) \cdot h\left(\frac{t-p}{3}\right)}{\Gamma(t+1)} (3z)^t dt$$

in which

$$H(t) = \frac{\Gamma(t/3+1/3) \cdot \Gamma(t/3+2/3) \cdot \Gamma(t/3+1)}{\Gamma\left(\frac{t-p}{3}+a_1\right) \cdot \Gamma\left(\frac{t-p}{3}+a_2\right) \cdot \Gamma\left(\frac{t-p}{3}+a_3\right)}$$

Using Stirling's formula and recalling (16), $H(t)$ can be expanded as a factorial series. Hence, using (8) we write

$$H(t) \cdot h\left(\frac{t-p}{3}\right) = \sum_0^s C_n \frac{\Gamma(t+1)}{\Gamma(t+n+1)} + \frac{\sigma(t, s) \cdot \Gamma(t+1)}{\Gamma(t+s+1)}$$

where the C_n 's are constants and $\sigma(t, s) = 0$ ($s = 0, 1, 2, \dots$) as $t \rightarrow \infty$ along any ray from $t = 0$ in the positive half of the t axis.

Hence we write

$$Q(z, l) = \frac{\sqrt{3}}{2\pi z^p} \left[\sum_0^s C_n \int_{p-l-\frac{1}{2}}^{\infty} \frac{(3z)^t}{\Gamma(t+n+1)} dt + \int_{p-l-\frac{1}{2}}^{\infty} \frac{\sigma(t, s) (3z)^t}{\Gamma(t+s+1)} dt \right] \quad (19)$$

Making use of Theorem II we get,

$$e^{3z} = \int_{p+n-l-\frac{1}{2}}^{\infty} \frac{(3z)^w}{\Gamma(w+1)} dw - \sum_1^L \frac{1}{\Gamma(1-n) z^n} + \delta(z, L)$$

where

$$\lim_{z \rightarrow \infty} z^L \cdot \delta(z, L) = 0 \text{ and } -\pi < \arg z < \pi,$$

and L denotes the greatest integer in $l - n - R(p) - 1/2$, the path of integration extending to infinity in the direction of the positive real axis of w . By proper choice of l , L may be made independent of n and we then get

$$\lim_{z \rightarrow \infty} z^n \cdot \delta(z, L) = 0 \text{ for } n = 0, 1, 2, \dots$$

Hence we get

$$\int_{p-l-\frac{1}{2}}^{\infty} \frac{(3z)^t}{\Gamma(t+n+1)} dt = \frac{e^{3z}}{(3z)^n} [1 + \theta(z, L)]$$

where $\lim_{z \rightarrow \infty} z^n \cdot \theta(z, L) = 0$ for $n = 0, 1, 2, \dots$

Thus the sum in (19) reduces to

$$e^{3z} \left[\sum_1^s \frac{C_n}{(3z)^n} + \frac{C_s \theta(z, L)}{(3z)^s} \right].$$

Also applying Theorem III the integral in (19) may be shown to be zero.

Thus

$$Q(z, L) = \frac{\sqrt{3} e^{3z}}{2\pi z^p} \left[\sum_0^s \frac{C_n}{(3z)^n} + \frac{\eta(z, s)}{(3z)^s} \right]$$

where $\lim_{z \rightarrow \infty} \eta(z, s) = 0$.

Using this result in (14) we finally get

$$f(z) \sim \frac{\sqrt{3} e^{3z}}{2\pi z^p} \sum \frac{C_n}{(3z)^n} - \sum \frac{h(-n/3) z^{-n}}{\Gamma(a_1 - n/3) \cdot \Gamma(a_2 - n/3) \cdot \Gamma(a_3 - n/3)}$$

when $-\pi/2 < \arg z < \pi/2$. Further we note that

$$z^{-p} e^{-3z} \cdot \sum \frac{h(-n/3)}{\Gamma(a_1 - n/3) \cdot \Gamma(a_2 - n/3) \cdot \Gamma(a_3 - n/3)} \cdot z^n$$

can be developed asymptotically in the form

$$0 + \frac{0}{z} + \frac{0}{z^2} + \dots$$

when $-\pi/2 < \arg z < \pi/2$. Thus we finally get

$$f(z) \sim \frac{\sqrt{3} e^{3z}}{2\pi z^p} \sum_0^\infty \frac{C_n}{(3z)^n}.$$

Substituting $z \cdot e^{2\pi i/3}$ and $z \cdot e^{-2\pi i/3}$ for z in (20) and summing the three expressions so obtained we get

$$F(z) \sim \frac{e^{3z}}{\sqrt{3} 2\pi z^p} \sum_0^\infty \frac{C_n}{(3z)^n}.$$

It will be clear that the region for which the expansion remains valid is $-\pi/6 < \arg z < \pi/6$.

The series (20), (21) and (22) required in the body of the paper are only particular cases of $F(z)$. Thus to get the asymptotic expansion of series in (20), we have

$$F(z) = \sum_n^\infty \frac{z^{3n}}{n \cdot \Gamma(n+1) \cdot \Gamma(n+1) \Gamma(n+1)}$$

Here

$$h(n) = 1/n, a_1 = a_2 = a_3 = 1, \text{ and hence } p = 1.$$

$$H(t) = \frac{\Gamma(t/3 + 1/3) \cdot \Gamma(t/3 + 2/3) \cdot \Gamma(t/3 + 1)}{\Gamma(t/3 + 2/3) \cdot \Gamma(t/3 + 2/3) \cdot \Gamma(t/3 + 2/3)}.$$

Now

$$\begin{aligned} \log \Gamma(x+h) &= \frac{1}{2} \log 2\pi + x \log x - x + B_1(h) \cdot \log x \\ &\quad - \sum (-1)^n \frac{B_{n+1}(h)}{n(n+1) x^n} \end{aligned}$$

where B 's are Bernoulli's polynomials of order n . Hence we get

$$\log H(t) = \frac{B_2(1/3) + B_2(1) - 2B_2(2/3)}{1 \cdot 2 \cdot t/3} + 0(1/t^2).$$

Using

$$B_2(h) = h^2 - h + 1/6$$

we get

$$\log H(t) = 1/3t + 0(1/t^2).$$

Hence

$$\begin{aligned} H(t) &= e^{1/3t + 0(1/t^2)} \\ &= 1 + 1/3t + 0(1/t^2). \end{aligned}$$

Therefore

$$H(t) h\left(\frac{t-1}{3}\right) = \frac{3}{(t-1)} + \frac{1}{t(t-1)} + O(1/t^3).$$

Converting the above into factorial series we get

$$H(t) h\left(\frac{t-1}{3}\right) = \frac{3}{t+1} + \frac{7}{(t+1)(t+2)} + O(1/t^3).$$

Thus

$$C_0 = 0, C_1 = 3, C_2 = 7, \text{ etc.}$$

Hence

$$F(z) \sim \frac{e^{3z}}{\sqrt{3} 2\pi z} \left[\frac{1}{z} + \frac{7}{9z^2} + O(1/z^3) \right]$$

Similarly the asymptotic expansions for (21) and (22) are obtained.

REFERENCES

1. Fisher, R. A. .. *On the Mathematical Foundations of Theoretical Statistics.*
2. Ford, Walter B. .. *Asymptotic Developments of Functions Defined by Maclaurin Series.*
3. Jeffries .. *Theory of Probability.*
4. Milne-Thompson, L. M. .. *The Calculus of Finite Differences.*

FLUCTUATIONS OF LIGHT INTENSITY IN CORONÆ FORMED BY DIFFRACTION

BY G. N. RAMACHANDRAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received September 22, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

THE problem of determining the resultant of the secondary radiations emitted by a cloud of similar particles under the action of a primary wave is an important one in the field of optics. It might be supposed that when there are a large number, n , of such particles, distributed at random, the resultant intensity is just n times that due to a single particle. The late Lord Rayleigh (1871), however, showed that this is far from being the case, and that the resultant in any particular trial may be anywhere between 0 and n^2 , and does not show any tendency to close upon the value n . He has also investigated (1880) the probability that the resultant intensity may lie between assigned limits of magnitude, and has derived an expression for the distribution of the resultant intensity.

In a general way, the existence of such fluctuations of intensity is illustrated by the well-known experiment of using a glass plate on which lycopodium powder is dusted as the diffraction screen, and viewing a source of light through it. The effects observed depend greatly on the size of the source and its spectral nature. Even as early as 1877, Exner observed the existence of radial streaks such as those shown in Fig. 3 (a), Plate I, when the corona is seen in white light. More recently, Laue (1916, 1917) and de Haas (1918) have observed the fluctuations in monochromatic light. In this case, the radial fibres reduce to a "mottled structure" of the type shown in Fig. 3 (b).^{*} Laue's studies led him to suppose that the phenomena could not be completely explained on the basis of classical wave-optics. This contention was disputed by de Haas, who performed further experiments supporting the view that the phenomena are explicable on wave-principles.

In this paper, some theoretical considerations are presented regarding the nature of the fluctuations, and experiments performed with a view to

^{*} This will hereafter be referred to also as the "fine-structure" or "structure" of the corona.

substantiate the theory are also described. It is found, as is shown below, that de Haas's explanation of the phenomena is inadequate, and does not go to the root of the problem. In particular, the Rayleigh statistical law of distribution of intensity has been quantitatively verified for the first time, making use of the fluctuations of intensity in the corona as the basis for measurement.

2. *The Nature of the Fluctuations in Monochromatic Light*

de Haas's explanation of the mottled structure consists in considering every pair of particles to give rise to a set of interference fringes crossing the field. These are superposed, and produce fluctuations of intensity. This explanation, however, is wholly inadequate. In fact, when the number of particles is very large, one must take the aggregate effect of *all* the particles into account and not merely the effect due to pairs of particles. Each particle gives rise to a corona of its own, and the resultant intensity in any direction is due to the collective action of the wave-fronts diffracted by all the particles in that direction.

The failure of the de Haas point of view may be brought out strikingly by the following analogy. Suppose we are considering the opposite case of a regular square diffraction grating, formed for example by a square mesh of wires. In this case, one may take each pair of meshes in the grating, and imagine it as giving rise to a set of interference fringes of the type imagined by de Haas. But, such a method gives us no idea at all of what the nature of diffraction pattern due to the complete grating would be. The latter could be determined only by taking the waves diffracted by all the meshes simultaneously into account and finding their total effect. In those directions in which all these waves reinforce, we get bright spots; while elsewhere we have dark areas.

In the same way, with the lycopodium powder also, one has to consider the waves diffracted by all the particles together. Each particle becomes the centre of secondary radiation, and in those directions in which the phase relations between the waves diffracted by the particles happen to be such that there is a large co-operative effect, there will be bright spots. Since the positions of the particles on the screen are unknown, one cannot determine the positions of these maxima of intensity; but it is easily seen that there must be a large number of such spots irregularly arranged in the field of view.

We now proceed to show that these spots are in fact as sharply defined as the original image of the source formed by a lens whose aperture is the same as that of the diffracting screen. Consider a point P in

the focal plane of the camera where due to the co-operative action of the waves from the various particles, we have a large intensity, say I_P . The amplitude at this point will be $u_P = \sum_1^n e^{ip_m}$ where p_m is the phase of the m th particle on the screen, and the summation is done for all the n particles present, it being assumed that the amplitude due to each particle is unity. Therefore,

$$I_P = \left(\sum_1^n \cos p_m \right)^2 + \left(\sum_1^n \sin p_m \right)^2 = n + \sum_{r=1}^n \sum_{s=1}^n \cos (p_r - p_s). \quad (1)$$

Consider now a neighbouring point P' . At this point, the phases of the waves from the various particles would be altered. Let the alteration of phase for the m th particle be δ_m . Then, the amplitude at P' is

$$u_{P'} = \sum_1^n e^{ip_m} e^{i\delta_m}, \text{ and the intensity is}$$

$$I_{P'} = \left[\sum_1^n \cos (p_m + \delta_m) \right]^2 + \left[\sum_1^n \sin (p_m + \delta_m) \right]^2. \quad (2)$$

This can be expressed in the form

$$I_{P'} = n + \sum_r \sum_s \cos (\delta_r - \delta_s) \cos (p_r - p_s) + \sum_r \sum_s \delta_r \sin (p_r - p_s).$$

If the δ 's are small, this can be put in the form

$$I_{P'} = \left[n + \sum_r \sum_s \cos (p_r - p_s) \right] + \sum_r \sum_s \delta_r \delta_s \cos (p_r - p_s) + \sum_r \sum_s \delta_s \sin (p_r - p_s). \quad (3)$$

The second term is negligible, since it involves second order terms, so that

$$I_{P'} - I_P = \sum_{r=1}^n \sum_{s=1}^n \delta_s \sin (p_r - p_s). \quad (4)$$

Now, $\sin (p_r - p_s)$ is of the same order of magnitude as $\cos (p_r - p_s)$, so that $\sum_r \sum_s \delta_s \sin (p_r - p_s)$ is of a lower order compared with $\sum_r \sum_s \cos (p_r - p_s)$ which is the order of I_P . Thus, if δ is small, $(I_{P'} - I_P)$ is small compared with I_P .

Now, if we denote by $\delta\phi$ the angular separation of P and P' , then the largest value of δ_r or δ_s is given by $\pi b \delta\phi / \lambda$, where b is the width of the diffraction screen, and λ the wave-length of light. It is evident from (4) that $I_{P'}$ does not sensibly differ from I_P over a range of values of $\delta\phi$ within which the largest of the δ 's does not exceed a fraction of 2π , and over this range of angles, the large intensity at P will persist. Putting the maximum value of the δ 's for this to happen as, say, $\pi/4$ one gets the width of the bright spot as

$$\delta\phi = \frac{1}{4} \frac{\lambda}{b}. \quad (5)$$

Thus, the angular width of the bright spot is of the order of λ/b . Now, it is well known that the diffraction image due to a lens of aperture b also extends over an angle of the order of λ/b , so that the bright spot at P will be of the same sharpness as an image of the source formed by a lens of aperture b .

The argument used in the above discussion is, however, not restricted to the case when the intensity at P is a maximum. Actually, it is true whatever may be the intensity at P, so that one sees that the corona must actually consist of spots whose extension is of the same size as that of the image of the source. We have proved above that these images would not be spread out by an extent more than the aperture of the lens, so that we must expect the fine-structure to consist of sharp and well-defined images of the original source distributed at random. They are in fact the spectra formed by the irregular arrangement of the sources of secondary radiation produced by the particles.

Another interesting result, regarding the number of such spots in the field of view, comes out of the above discussion. As already remarked, the extent of the individual spots is given by the width of the aperture. Thus, we may divide the whole field of view into a number of areas, each of which is occupied by one spot. Now, on increasing the aperture, the area occupied by a spot decreases, so that more spots must appear in the field of view. To observe this phenomenon, the source of light must be small enough, so that the spots do not sensibly overlap. Otherwise, the fluctuations of intensity would all be wiped out by the overlapping, and the individual spots could not be discriminated. Under favourable conditions, however, the argument shows that the density or the number of spots per unit area must depend on the aperture employed, increasing with increase of its dimensions.

3. Experimental Confirmation

The verification of the above two deductions from the theory was done by the following experimental arrangement. The source of light, S (Fig. 1) was a pinhole, or an aperture of any size and shape as desired, which was illuminated by the filtered mercury radiation of 5461 Å. U. At a certain distance from the source was placed a glass plate G, on which lycopodium powder was dusted. The resulting diffraction pattern could be brought to a focus on a plate C by a lens L. An aperture AB was placed in front of the lens, and its size and position could be adjusted. When necessary, the camera could be removed and the pattern directly viewed with the eye.

Initial visual observations using a small circular hole as the source showed that the spots in the corona are also all circular in shape and of the

same size as the original source. On increasing or decreasing the size of the pinhole, the spots in the field of view also correspondingly became larger or smaller showing that they are images of the source. But the most convincing proof of this fact was obtained by using a triangular slit as the source, when every one of the spots assumed a triangular shape, and besides had the same size and orientation as the source. Photographs were then taken to illustrate this fact. They are reproduced in Fig. 4 (a) and (b), Plate I. Fig. 4 (a) was taken with a circular pinhole as the source, and Fig. 4 (b) with a triangular slit. They show in an unmistakeable manner that the spots are in reality images of the source.

The second conclusion from the theory was also verified by observation. On increasing the area of the aperture, it was found that the number of spots in the field of view increased, and *vice versa* as demanded by the theory.

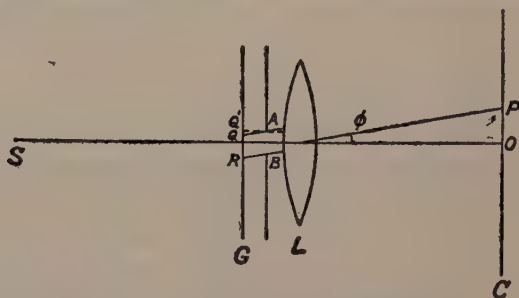


FIG. 1. Experimental Arrangement

During these experiments, a few other interesting phenomena were observed which also find a ready explanation on the idea that the spots are the spectra produced by the collective diffraction by all the particles.

(a) If one moves the screen containing the lycopodium powder keeping the eye fixed on the source, then the ring system is not found to undergo any change, but the fine-structure appears to move relative to the pattern of rings in the same direction as the motion of the screen. *Vice versa*, keeping the screen fixed, if one moves the eye, all the while looking at the source, then the fine-structure appears to move in a direction opposite to the motion of the eye. This effect is only the converse of the previous one. Also, if the screen is rotated, the fine-structure appears to rotate in the same direction.

These effects can be explained as being purely due to the geometry of the arrangement. Since the pupil of the eye is small, the whole of the screen does not contribute to the diffraction pattern nor is every portion of the pattern produced by the same portion of the screen. If we consider the corona in a direction ϕ (Fig.1), the intensity in this direction is due only to the waves diffracted by the region QR of the screen. Hence, if the screen is moved up, the

same portion QR is now responsible for the corona in a direction ϕ' parallel to Q'A. This happens for every portion of the screen, so that the fine-structure as a whole appears to move in the same direction as the screen relative to the rings. The effect of rotation is too obvious to need an explanation.

(b) During these experiments, it was found that the fine-structure not only moved bodily in the same direction as the motion of the screen, but that there were some internal changes as well. To follow these, the bodily motion was avoided in the following way. The aperture AB was placed in contact with the screen, and the lens L of the camera was large enough so that the whole diffraction pattern was caught by it. In this way, the difficulty of different portions of the screen giving rise to different portions of the corona was overcome. The whole of the screen was always operative. Now, on moving the screen in its own plane, the fine-structure pattern at the focal plane of the lens did not show any bodily movement; but there was an internal rearrangement of the spots.

This phenomenon could be explained as due to the fact that spherical waves are incident on the screen so that, on moving the screen in its own plane, the phase of the wave falling on each particle is altered. Thus, the phase relations between the waves emitted by different particles are changed, which leads to a change in the pattern of the spectra given by the particles and hence to a random rearrangement of the spots.

It is obvious that these internal changes must vanish if the incident wave is plane, for then a movement of the plate in its own plane should produce no change in the phase relationship between the different particles. This was tested out experimentally and it was found that with parallel light incident on the screen, the fine-structure pattern at the focal plane of the lens was entirely unaffected by moving the screen in its own plane. This shows that the explanation given above for the internal motion of the spots is correct.

(c) The phenomenon of the internal rearrangement of the spots can be observed with the eye also, if the aperture AB is made sufficiently small. In this case, on moving the aperture over the screen, different portions of the screen are operative, and since the arrangement of the particles in these are different, the spots in the field of view exhibit a beautiful "dance". The appearance is somewhat similar to that of the field of a spinthariscopes, with bright spots appearing and disappearing at random positions.

4. Fluctuations in White Light

We have already shown how, in monochromatic light, the fine-structure consists of a series of images of the source. We now proceed to investigate

what happens if white light is used. Suppose that, with monochromatic light of wavelength λ , there is a bright spot at P, in the direction ϕ (Fig. 1). In the diffracting screen, draw the X-axis parallel to OP, and the Y-axis perpendicular to it, and let (x_m, y_m) be the co-ordinates of the m th particle on the screen with respect to these axes of co-ordinates. Then, (supposing the incident wave to be plane) the intensity in the direction ϕ is equal to

$$\left| \sum_{m=1}^n e^{i k x_m \sin \phi} \right|^2 \quad (6)$$

where k stands for $2\pi/\lambda$. Now, supposing the wavelength of the light to be changed to λ' , and that $k' = 2\pi/\lambda'$, then it is readily seen from the above expression that the value of the intensity is unaltered provided we change ϕ to ϕ' , such that

$$k \sin \phi = k' \sin \phi', \text{ or } \sin \phi / \lambda = \sin \phi' / \lambda'. \quad (7)$$

Hence, the bright spot, which was formerly at P, would now appear at another point P' in the direction ϕ' given by expression (7) such that P' lies along OP. This argument also is not restricted to the case when P is a bright spot, but is quite general. Hence, with an increase in the wavelength of the light, the whole pattern expands radially so that to every point P in the first case there is one, P', in the second, such that

$$\frac{OP}{\lambda} = \frac{OP'}{\lambda'}. \quad (8)$$

If white light is used, there will be a range of wavelengths, so that there will be no discrete spots, but each spot will be spread out into a radial streak, whose colour is violet at the inner end and red at the outer end. The length of every such streak will be directly proportional to its distance from the centre, the streaks further away from the centre being longer.

As already remarked, such radial fibres were actually observed in white light by Exner. The author has observed these carefully and has found that one can actually follow the spectral colours in the order violet to red in any single fibre, as one goes away from the centre. Very close to the centre of the field, however, one can observe a few white spots, since the dispersion in them is very small on account of their proximity to the centre. The length of the fibres (the distance from the violet to the red end) is found to be proportional to their distance from the centre, and the length of any fibre at a certain distance is found to be a constant, within the limits of the experimental error.

In order to further demonstrate the correlation between the spots in monochromatic light, and the fibres in white light, the following experiment

was performed. A pointolite lamp was used to illuminate a fine pinhole, and a mercury green filter supplied by Adam Hilger & Co., was interposed. This transmitted only two bands, one in the green and the other in the red. The fine-structure now presented a beautiful appearance. The pattern was filled with red and green spots; but every green spot was accompanied by a red one, the two being along a radius, and the red spot being the outer one. It was also verified that the ratio of the distances of the red and the green spots from the centre was a constant, and was equal to the ratio of the mean wavelengths of the red and green transmission bands.

5. *Verification of the Rayleigh Law of Fluctuations*

Lord Rayleigh (1880) derived an expression for the distribution of intensity in the resultant due to n vibrations whose phases are at random. If the amplitude of a vibration is taken as unity, and as a special case, if the phases are assumed to have only either of values 0 or π , then it follows directly from Bernoulli's theorem that the chance of a positive amplitude between x and $x + \delta x$ is $\frac{1}{\sqrt{2\pi n}} e^{-x^2/2n} \delta x$. In the more general case of arbitrary phase, the probability that the resultant amplitude may lie between r and $r + \delta r$ comes out as

$$\frac{2}{n} e^{-r^2/n} r \delta r. \quad (9)$$

From this, it follows that the probability that the intensity may be between I and $I + \delta I$ is

$$p(I) \delta I = \frac{1}{n} e^{-I/n} \delta I. \quad (10)$$

We can put this in a more convenient form. From (10), it can be shown that the average value of the intensity is n . Expressing I as a fraction f of the average value, i.e., putting $I/n = f$, (10) reduces to

$$p(f) \delta f = e^{-f} \delta f. \quad (11)$$

This gives the probability that the resultant intensity may lie between the fractions f and $f + \delta f$ of the average, and is the same function for all values of n . It is a maximum for $f=0$, and decreases as f increases.

This law can be verified by making use of the fine-structure in the corona. As already said, the fine-structure is produced as a result of the interference of the light diffracted by all the powder grains. The relative phases of these diffracted waves are not known but are distributed at random. Also, for different angles, ϕ , the phase relations are different, so that the whole pattern actually presents the effect of different combinations of these phase relations.

Hence, the resultant intensity in the pattern must show the same statistical law of fluctuations as demanded by Rayleigh's theory.

This was verified in the following way. A very fine pinhole illuminated by the mercury green radiation of 5461 Å.U. was used as a source of light, and a picture of the central portion of the corona was taken with an exposure of two hours on a Selochrome plate. To obtain a standard of intensities, a square grating was used instead of the lycopodium screen, and the same exposure was given for the grating also. The grating gave a spectrum, the intensities of whose spots are calculable. The plates for the two photographs were obtained by cutting a single quarter plate into two. Both were developed simultaneously in the same developing bath for the same time. Thus, a strictly comparable scale of intensities was obtained for determining the intensity of the spots in the corona. The photographs of the corona and the standard grating spectra are reproduced in Fig. 5 (a) and 5 (b), Plate I, respectively.

Now, in the corona, the average intensity falls away from the centre in the proportion $J_1^2(x)/x^2$ where $x = 2\pi a \sin(\phi)/\lambda$, a being the radius of the particle, ϕ the angle of diffraction, and λ the wavelength of the light. The corona taken in the present case extended upto a value of $x = 1.5$, for which the average intensity was about half that at the centre. It was therefore divided into annular rings, the widths of which were all equal to $x = 0.25$, by drawing circles of radii corresponding to $x = 0.25, 0.5$ etc. Within each ring, the value of $J_1^2(x)/x^2$ did not vary much, and the average value for a ring was taken to be correct for that ring.

Using the grating spectrum, the intensity of whose spots could be calculated, an arbitrary scale of intensities was obtained. Then, the spots in each ring were classified into this scale, comparing them visually with the standard. The spots having an intensity less than 1 in the arbitrary scale, *i.e.*, those that could not be differentiated with the eye were found by calculating the total number of spots (dividing the area of the ring by the area of a spot) and subtracting from this the number of counted spots. Using this tabulated list, the average intensity (on the arbitrary scale) for that ring could be determined. Thus, the fraction of the total number of spots having an intensity between the fraction f_1 and f_2 of the average could be found. Dividing this by $(f_1 - f_2)$ we get the value of $p(f)$ at $(f_1 + f_2)/2$. Thus, $p(f)$ was evaluated for certain values of f . This was done for four rings, *viz.*, $x = 0.25$ to 0.50 , 0.50 to 0.75 , 0.75 to 1.00 , and 1.00 to 1.25 . These were plotted in a graph and are reproduced in Fig. 2. The continuous curve represents the theoretical curve calculated from theory, and the experimental values are plotted by points.

A final average of all these four rings was obtained by dividing the intensities of the spots in each by the value of $J_1^2(x)/x^2$ for it, and then determining $p(f)$ and f taking them all into account. These are tabulated in the table below, and are represented by black dots in Fig. 2. It is clearly seen that the experimental points fit the theoretical curve very well, considering

f	$p(f)$	Theoretical	Difference
0.44	0.60	0.62	-0.02
1.29	0.33	0.28	+0.05
2.13	0.14	0.12	+0.02
3.45	0.02	0.03	-0.01
6.25	0.002	0.002	..

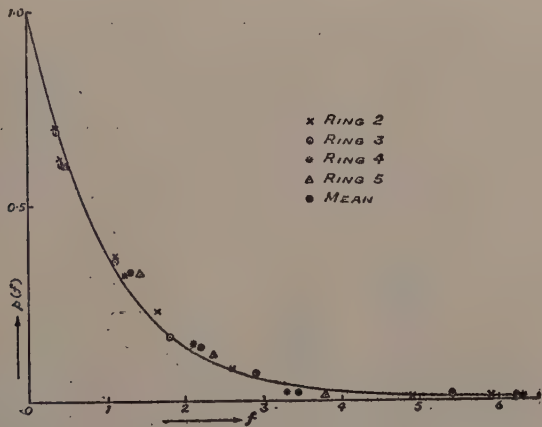


FIG. 2. Verification of Rayleigh's Statistical Law

that the comparison of intensities was done visually. Rayleigh's formula is therefore verified to be true for the distribution of intensity in the corona.

6. Conclusion

The above considerations regarding the fluctuations of intensity are true only for a static diffraction screen, *i.e.*, one in which the phase relations between the various particles is fixed in time. If the particles themselves are in motion, as in a gas or a cloud, then a continuous redistribution of phase takes place, and what one sees is the integrated effect of all these over a definite period. As Lord Rayleigh (1918) has shown, such a redistribution tends to make the resultant intensity (perceived as an average over a certain period) approach the average value n , this tendency being greater the larger the number of redistributions. Hence, for the light scattered by a gas, or a

cloud of particles, one is quite justified in regarding the scattered intensity in inclined directions as equal to n times that due to a single particle.

If the motion of the particles is slow, then the alteration in the position of the spots in the fine-structure will also be slow, and can be observed. Such a slow random motion takes place in Brownian movement, so that it must be capable of detection by this technique. This possibility, which was suggested by Prof. Sir C. V. Raman, is now under investigation.

I wish to express my sincere thanks to Prof. Sir C. V. Raman for suggesting the problem, and for the many helpful hints he gave during the investigation.

7. Summary

The fluctuations of light intensity in the diffraction corona produced by a large number of randomly distributed particles are investigated both theoretically and experimentally. The theoretical considerations show that the view put forward by de Haas is inadequate and that really the fluctuations arise owing to the interference of the waves diffracted by *all* the particles, which gives rise to a large number of sharp images of the source in monochromatic light. In white light, these spots must spread out, and produce radial streaks. These deductions from theory are all borne out by experiment.

Making use of the fluctuations of intensity in monochromatic light, verification has been made for the first time of Rayleigh's statistical law of distribution of intensity in the resultant of n vibrations of arbitrary phase. It is shown that the resultant intensity shows no tendency to close upon the average value, n , but that it is distributed over a wide range of values.

REFERENCES

1. de Haas, W. J. .. *Proc. K. Akad., Amsterdam*, 1918, 20, 1278.
2. Exner .. *Sitzungsber. Akad. Wien*, 1877, 76, 522.
3. Laue, von .. *Phys. Gesselsch., Zürich*, 1916, 90.
4. ——— .. *Berichte deutsch. Phys. Gesselsch.*, 1917, 19, 19.
5. Rayleigh, Lord .. *Proc. Lond. Math. Soc.*, 1871, 3, 267.
6. ——— .. *Phil. Mag.*, 1880, 10, 73.
7. ——— .. *Ibid.*, 1918, 36, 429.

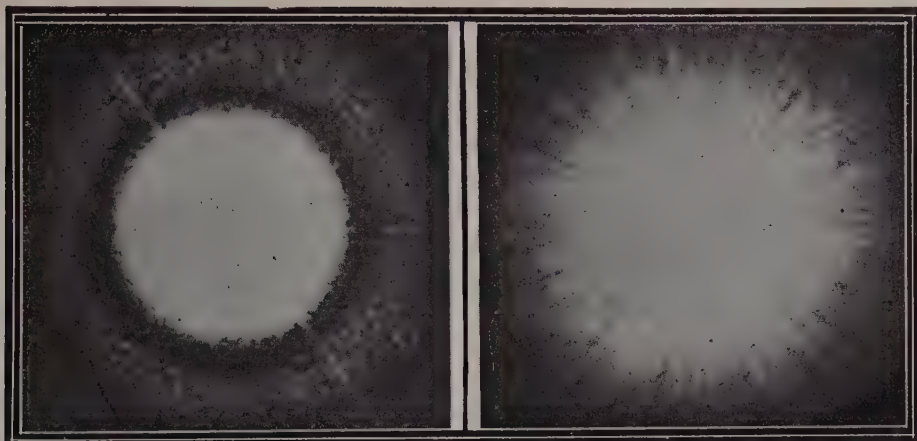


FIG. 3(a)

FIG. 3(b)

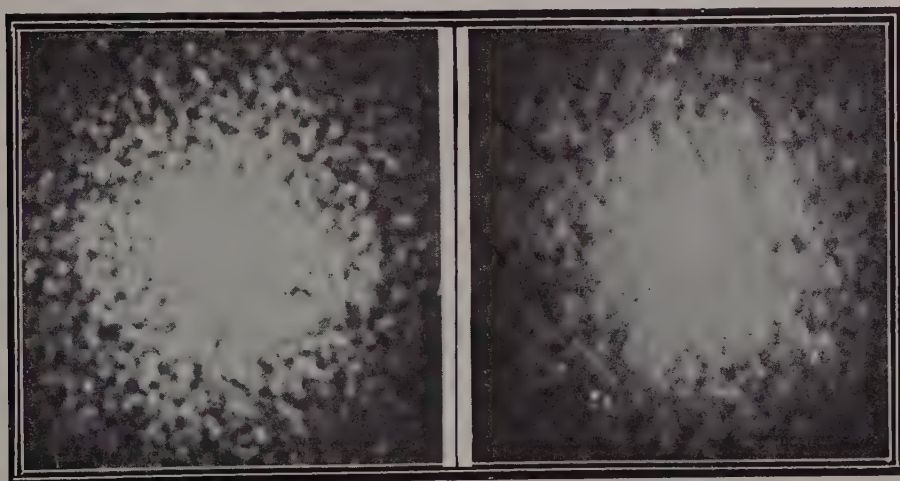


FIG. 4(a)

FIG. 4(b)

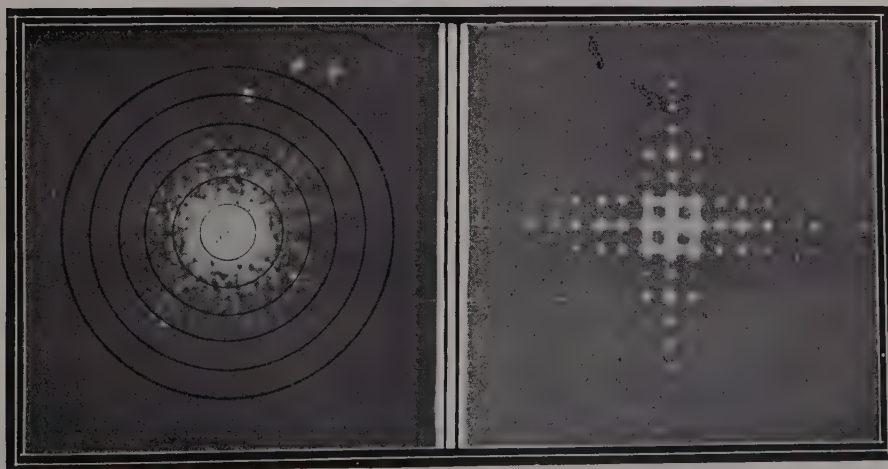


FIG. 5(a)

FIG. 5(b)

CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part IV. A Note on the Bitter Principle of a Variety of *Citrus limetta*

BY T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair, now at Madras)

Received August 25, 1943

A VARIETY of *Citrus limetta* available in the northern and north-western parts of India during the hot weather has certain peculiar characteristics. It is quite juicy and the juice when carefully sucked out is almost insipid having only a faint sweet taste. But if the fruit should be crushed leading to pressure on the rags, the juice becomes exceedingly bitter. The bitter principle is present mainly in the rags. The thin peel, which is rather difficult to remove is not so bitter. The seeds are very small. The external appearance of the fruits is quite similar to that of the sweet variety of *Cirtus limetta* (mussambi) common in Central and Western India and both go by the same common name, Mitta. The rind is yellow to orange in colour and smooth.

A fruit weighs on an average 200 grams and the juice yield is 100 to 120 grams (50 to 60%). The peels constitute 12–15%, the fresh rags 25–30% and the seeds about 0.7% of the fruit. The results of analysis of juice (average of several experiments) is as below: Brix 8.3°, reducing sugars 6.3%, total sugars 6.3%, sucrose nil, acidity 0.01% as citric acid. Thus there is very little acid and though the sugar content is not very low, sucrose is absent and consequently sweetness is poor.

The bitter principle was extracted from the rags by repeated treatment with cold alcohol and the extract concentrated to small bulk. With a view to detect the existence of more than one crystalline entity, the solid matter was isolated in fractions and then purified. By the addition of an equal volume of water to the alcoholic concentrate fraction (I) was obtained. Concentration of the mother-liquor during which most of the residual alcohol was evaporated, yielded fraction (II). The final mother-liquor (M) was separately examined. When fraction (I) was extracted with excess of boiling acetone, most of it dissolved leaving behind a very small quantity of resinous matter. On allowing the solution to concentrate a crystalline solid was obtained (fraction I A). Addition of water to the mother-liquor yielded an amorphous solid (fraction I B). Fraction (II) was also soluble in acetone and from it fractions (II A) and (II B) were obtained.

Fraction (I A) was insoluble in water, sparingly soluble in alcohol and readily soluble in acetone. It was best crystallised from acetic acid from which it came out as colourless rectangular prisms and tablets. The substance charred and burnt when introduced into a flame and left no residue. It melted at $292-94^{\circ}$ with decomposition. When an alcoholic solution of it was treated with magnesium and hydrochloric acid no red or orange colour was developed. A dilute aqueous alcoholic solution was quite bitter; $[\alpha]_D^{30}, -115.1^{\circ}$ in acetone solution. From these properties it seemed to be limonin and this surmise was confirmed by careful comparison with an authentic sample of limonin obtained from the seeds of Indian shaddock¹ and determination of the mixed melting point. Fractions (I B), (II A) and (II B), when subjected to crystallisation, yielded the same product thereby showing that there was only one bitter principle in all of them.

The aqueous mother-liquor (M) was made 7% acid with sulphuric acid and boiled for 2 hours. To start with there was a clear solution and at the end a dark brown resinous solid was found to have separated out. It was almost insoluble in acetone and an alcoholic extract (sparingly soluble in alcohol) gave no colour with magnesium and hydrochloric acid. No crystalline substance could be isolated from it. Thus the absence of naringenin in the resinous matter and of naringin in the aqueous mother-liquor was established.

Consequently the only crystalline bitter principle of the above variety of *Citrus limetta* is limonin. This bitter substance has been formerly found to occur mainly in the seeds of the lemon, oranges and shaddock and it is invariably accompanied by more or less quantities of the closely related compound, isolimonin.^{2,1}

It seems to be now clear that these complex bitter compounds of unknown constitution contribute also to the bitterness of the rags and peels of certain types of oranges. Isolimonin has been found by Higby³ to be the main bitter component of the peels and rags of American Navel oranges and limonin to be present in the pulp of Valencia oranges. The present note records a further case of this kind. The constitution of limonin is quite indefinite. But its formula seems to be definite as $C_{26}H_{30}O_8$. Since the number of carbon atoms is near those of sterols and resinols, its reactions with the special reagents of these groups of compounds has now been studied. With the Liebermann-Burchard reagent it yields a very pale yellow solution. On the other hand, with the Salkowski reagent, the chloroform layer is colourless with a weak bluish violet fluorescence and the sulphuric acid layer first turns

yellowish brown and in the course of a few minutes becomes deep brown red. These characteristics are different from those of sterols and of resinols.

Summary

A variety of *Citrus limetta* has been found to contain limonin as the only bitter principle of the rags. The characteristics of the fruit and its juice are described.

REFERENCES

1. Seshadri and Veeraraghaviah .. *Proc. Ind. Acad. Sci.*, 1940, **11 A**, 505.
2. Köller and Czarney .. *Monatsh*, 1936, **67**, 248 ; 1937, **70**, 26.
3. Higby .. *J.A.C.S.*, 1938, 3014.

PIGMENTS OF COTTON FLOWERS

Part IX. A Note on the Occurrence of Populnetin in Indian Cotton Flowers

BY P. SURYAPRAKASA RAO AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair, now at Madras)

Received September 8, 1943

IN the course of their study of the colouring matter of the flowers of *Gossypium indicum*, Neelakantam and Seshadri reported the isolation of a new non-glycosidic compound.¹ The total pigment of the flowers was separated into five fractions according to the general scheme and studied. The first alcohol fraction contained mainly gossypin, a complex glycoside of gossypetin and the second (aqueous) fraction gave a small amount of the new substance which was not given any name at that time since it could not be studied in detail and its individuality was not quite definite. In the course of our examination of various samples of *G. herbaceum* flowers this substance has been again met with in small quantities and hence it occurs in this source also. Its main characteristics are (1) stability to aerial oxidation in alkaline solution thus indicating that it is a flavone, (2) lack of any colour changes in buffer solutions of pH on the alkaline side, (3) dissolution in concentrated sulphuric acid forming a yellow solution with a bright green fluorescence, (4) absence of any precipitate when an alcoholic solution is treated with neutral lead acetate, (5) formation of a yellow precipitate with basic lead acetate and (6) absence of methoxyl in its composition. These seemed to indicate that it was probably populnetin² and the idea was supported by the fact that populnetin occurs along with herbacetin in the flowers of *Thespesia populnea*³ and hence could be expected to accompany it in the Indian cotton flowers also. But the melting point of the substance was rather low and the results of analysis were not definite due probably to the presence of inseparable impurities and the existence of hydration which seemed to vary with different conditions. The preparation and study of the acetyl derivative were not more helpful. The quantity available after these experiments was too small for further repeated purification and a detailed study independently. Consequently it was subjected to complete methylation using an acetone solution and excess of dimethyl sulphate and dilute sodium hydroxide. The product could be crystallised from alcohol from which it came out in the form of rectangular plates which were almost colourless. In its melting point, reactions and analysis, it was found to be identical with a sample of tetramethyl populnetin (described below) obtained by methylating an

authentic sample of populnetin isolated from *T. populnea*. It appears that definite purification is effected during methylation leading to the isolation of a pure methyl ether. The non-glycosidic substance should therefore consist mostly of populnetin.

Methylation of Populnetin

The flavone (1 g.) was dissolved in acetone (40 c.c.) and treated alternately in small quantities with 10% aqueous sodium hydroxide (50 c.c.) and dimethyl sulphate (10 c.c.). Finally the medium was made alkaline by the further addition of the alkali (50 c.c.) with vigorous shaking. In an hour an almost colourless crystalline compound separated out. It was filtered and recrystallised from alcohol using a little animal charcoal. Under the microscope it appeared as rectangular plates which were almost colourless. On heating it shrank at 95–100° (dehydration) and melted at 164–66°. It was insoluble in dilute alkali and did not yield any colour with ferric chloride. Its solution in concentrated sulphuric acid had a weak green fluorescence. [Found in the air-dried sample: C, 60.6; H, 6.2, and loss (H_2O) on heating at 110° for 2 hours *in vacuo*, 9.2%. $\text{C}_{15}\text{H}_6\text{O}_2 (\text{OCH}_3)_4, 2\text{H}_2\text{O}$ requires: C, 60.3; H, 5.8 and H_2O loss, 9.5%. Found in the dehydrated sample: C, 66.2; H, 4.9%; $\text{C}_{15}\text{H}_6\text{O}_2 (\text{OCH}_3)_4$ requires C, 66.6; H, 5.2%.] The mixed melting point with the methyl ether obtained from the sample derived from the cotton flowers was undepressed.

From the experiments described above it is clear that populnetin occurs free in the Indian cotton flowers along with gossypetin, herbacetin and quercetin which are present mostly as glycosides. Thus there is a further case of the association which was first found in the flowers of the *Thespesia populnea*. It has already been shown that the substance is a tetrahydroxy flavone having a hydroxyl in the 4'-position. The disposition of the other groups in the benzopyrone part is still a matter of investigation. Its occurrence along with compounds having the 5:7:8-orientation of hydroxyls seems to suggest a similar disposition of the hydroxyl groups in it also.

Summary

The new non-glycosidic substance obtained from the Indian cotton flowers has been shown to consist mostly of populnetin from a comparison of the methyl ethers. The characteristics of the methyl ether of populnetin are described.

REFERENCES

1. Neelakantam and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1936, **4**, 54.
2. Neelakantam, Rao and Seshadri *Ibid.*, 1943, **17**, 26.
3. Rao and Reddy .. *Ibid.*, 1940, **12**, 372.

CHEMICAL EXAMINATION OF INDIAN ERGOT OF THE NILGIRIS

BY S. RANGASWAMI AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair, now at Madras)

Received August 25, 1943

SOME time back Thomas and Ramakrishnan¹ described their very successful experiments on the production of ergot of rye in the Nilgiris. Mr. Thomas sent us a sample as early as October 1942. We intended to make a detailed study of it as the first sample grown under Indian conditions and obtain information regarding the influence, if any, of habitat on the chemical composition. Owing to serious difficulties which we then had of laboratory and library we could not undertake the complete examination immediately; but after a proximate analysis the material was defatted and preserved. Further examination was carried out in March 1943 and the results were not without interest. Meanwhile Mukherji and Dey² published their note on the assay of Indian ergot and expressed their opinion that the Nilgiris ergot was at least of the British Pharmacopœial quality, if not better. Our results indicate that our sample is really of very high quality comparing favourably with the richest ever produced in different parts of the world and hence they are presented here.

Proximate analysis of the entire drug by standard methods gave the following values; the values reported by previous workers and taken from Barger's book on 'Ergot and Ergotism'^{3a} are given within brackets for comparison.

Moisture	7.9% (4.4—10.0)
Ash	3.0% (2.2—7.0 ; average 4.0)
Total Nitrogen	3.57%
Fat (Petroleum ether extract)	27.3% (21.0%)

The fat which was a liquid had the following characteristics ; the figures within brackets have the same significance as above.

Refractive index at 32° C. ..	—1.466 (1.4685—1.4739 at 20° C.)
Saponification value ..	196.2 (178.4—196.9)
Iodine value (1—hour Wij's)	—72.9 (69.55—73.8)
Unsaponifiable matter ..	1.7% (0.35—1.04; average 1.0)
Hehner number	96.5 (96.0—96.3)

The rest of the sample of ergot was powdered, defatted thoroughly with petroleum ether (boiling range 40–50°) by percolation, dried in the air and preserved in an air-tight container. The alkaloidal assay was carried out by the method of Hampshire and Page⁴ as described in Garratt's book *Drugs and Galenicals*.⁵ 7.0 gm. of the defatted sample were taken for the assay. The rest of the procedure was in general according to the description given in the above-mentioned reference except that a slightly larger volume of 1% tartaric acid was used for extracting the alkaloids from ether solution and the final tartaric acid solution had to be rediluted to give an easily measurable intensity of colour with the special alkaloidal reagent prepared according to the 1936 Addendum to the 1932 B.P. The concentration of alkaloids was obtained by using the Lovibond Tintometer of the B.D.H. pattern for measuring the intensity of colour. When the colour was developed using 1 ml. of the above solution and 2 ml. of the reagent, 8 blue units on the Lovibond Tintometer were taken to represent a concentration of 0.0001 gm. of anhydrous ergotoxine per ml. (*vide* Garratt, p. 112). The following values were obtained: Total alkaloids as anhydrous ergotoxine 0.585%; water-insoluble alkaloids as anhydrous ergotoxine 0.417%; water-soluble alkaloids as ergometrine 0.090%. The last figure was calculated by using the relation obtained by Hampshire and Page (*loc. cit.*) between ergotoxine and ergometrine, *viz.*, that the colour equivalent of ergometrine is 1.86 times that of ergotoxine. All the above figures are with reference to the defatted ergot sample. The corresponding values calculated on the original ergot sample will be 0.425, 0.303 and 0.0654% respectively.

In the meanwhile the note of Mukherji and Dey (*loc. cit.*) appeared in *Current Science* reporting values as low as 0.1213% for total alkaloids and 0.0237% for water-soluble alkaloids, based on the results of analysis by the same chemical method of Hampshire and Page and confirmed by pharmacological assays. With a view to see if our high value was due to any errors in the technique or in the assumed relation between ergotoxine content and blue value the sample was reassayed according to the standard method of 1932 B.P. modified by the 1936 Addendum. However, in view of our previous high results only 2.0 gm. of defatted ergot powder was taken. The rest of the procedure was according to the B.P. The total volume of the tartaric acid solution used in the extractions of the alkaloid from ether solution finally amounted to 52 ml. and this solution was further diluted with an equal volume of 1% tartaric acid for convenient colour matching. The comparison was done against a freshly prepared solution of ergotoxine ethanesulphonate taken from a freshly opened sealed tube of the compound procured from Messrs. B.D.H. and a Duboscq type of colorimeter was employed. The

value for total alkaloids obtained by this method was 0.465% as anhydrous ergotoxine calculated with reference to the defatted ergot and 0.338% on the entire ergot. It is well known that the B.P. method of assay includes only a portion of the water-soluble alkaloids.

The standard solution of ergotoxine ethanesulphonate was also utilised for checking the accuracy of the tintometric colour relation with the alkaloid content. Careful readings showed that the tintometer used in the previous assay entirely satisfied the colorimetric relation. 0.0001 gm. of anhydrous ergotoxine contained in 1 ml. of solution gave with the standard reagent under standard conditions a colour whose blue component was 8 units; so that the previous assay using only the tintometer for the evaluation of the total and water-soluble alkaloids was entirely correct.

Thus it is obvious that the sample of ergot examined by us is very rich in alkaloid content. There is nothing improbable in this high value. In his well-known book Barger^{3b} gives numerous data for the alkaloidal content of various samples as obtained by different workers. Therein values as high as 0.38 and 0.414% are found for certain samples. More recently Bekes⁶ has reported a value as high as 0.74% obtained in the course of large-scale experiments on the intensive production of rye-ergot. The same author has also studied the alkaloidal content of individual sclerotia⁷ and reported values as high as over 1% of total alkaloids with several samples. It should however be noted that variations are possible in the qualities of the samples depending on differences in the conditions of collection and preservation and this may account for the differences between our results and those of others.

In any project for the production of ergot adequate precaution has to be taken to prevent infected rye grains finding their way into those collected for food, since ergot is a poison. A reliable chemical test for the presence of ergot makes use of the colour reaction for sclererythrin which is a crimson violet colouring matter present in the walls of the cortical hyphæ, probably as the calcium salt. The test was carried out as below with the present sample of ergot: About 0.1 gm. of the powdered ergot was shaken with 5 ml. of ether and a few drops of dilute sulphuric acid for 5 minutes. The ether solution was then decanted, diluted to 10 ml. and half the volume treated with 2 ml. of a saturated solution of sodium bicarbonate. A deep violet colour was formed in the aqueous layer. This colour test shows that the Nilgiris ergot easily conforms to the ordinary requirements of ergot for purposes of testing food grains.

Summary

A sample of Indian ergot of the Nilgiris has been studied in detail. It contains remarkably high percentage of total and water-soluble alkaloids. With respect to other components it is normal.

REFERENCES

1. Thomas and Ramakrishnan .. *Mad. Agr. J.*, 1942, **30**, 411.
2. Mukherji and Dey *Current Science*, 1943, **12**, 87.
3. Barger *Ergot and Ergotism*, Gurney and Jackson, 1931 ;
a. pp. 141-5 ; b. pp. 204-5.
4. Hampshire and Page .. *Quart. J. Pharm.*, 1936, **9**, 60.
5. Garratt *Drugs and Galenicals*, Chapman and Hall, 1937, pp. 112-4.
6. Bekesy *Biochem. Z.*, 1940, **103**, 5-6, 368-383.
7. ————— .. *Ibid.*, 1940, **102**, 3-4, 187-197.

INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN BINARY LIQUID MIXTURES: PART I

BY K. SUNANDA BAI

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received October 12, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

THE blue opalescence of binary liquid mixtures in the vicinity of their critical solution temperature has been the subject of numerous investigations in the past. Smoluchowski (1908) was the first to put forward a thermodynamic explanation of this phenomenon as due to optical inhomogeneity caused by spontaneous local fluctuations in concentration in the mixture. Einstein (1910) extended this theory with certain simplifying assumptions, namely (1) that the liquids are incompressible; (2) that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them; and (3) that the latter can be treated as ideal gases and on this basis derived an expression for the intensity of the opalescent light. This theory predicts an infinite intensity of scattering and also complete polarisation of the scattered light at the critical solution temperature. Experimental investigations of the opalescent light by several authors however showed that as the critical solution temperature is approached neither does the intensity of scattering tend to infinity nor is the polarisation of the scattered light perfect. In order to explain these difficulties Ornstein and Zernike (1914, 16, 18, 26) put forward a modified theory which considered the mutual influence of fluctuations in composition in neighbouring volume elements and according to which the intensity assumes a finite value at the critical temperature and is proportional to λ^{-2} and not to λ^{-4} as given by the formula of Smoluchowski-Einstein.

In order to explain the persistence of the opalescent phenomenon over a wide range of temperatures accompanied by remarkable changes in intensity and state of polarisation Raman and Ramanathan (1923) revised Einstein's theory taking into account the compressibility of the mixture and the varying orientations of the molecules. According to them the total intensity of light scattered by liquid mixtures is the aggregate of the separate effects of (1) fluctuations in concentration of the mixture, (2) fluctuations of its density and (3) the varying orientations of the anisotropic molecules.

Einstein's theory ignores the latter two effects which become of increasingly greater importance relative to the first at temperatures above or below the critical solution temperature.

The earlier investigators in this field suggested as an explanation of the opalescence before the thermodynamic explanation was put forward by Smoluchowski that the liquid mixture in the vicinity of the critical solution temperature behaves as an emulsoid. That this suggestion is not altogether baseless has been shown by Krishnamurti (1929) who found in X-ray diffraction studies with liquid mixtures that there are in general two types of liquid mixtures, one giving two separate rings for the two components and the other giving mainly one ring. The partially miscible liquids below their critical temperatures are found to belong to the first type and completely miscible liquids to the second type. The tendency for the formation of two distinct rings is explained by him by postulating the formation of large molecular clusters of the individual components. Recently Krishnan (1935) by means of a delicate optical method has shown that the molecules of critical composition mixtures in the neighbourhood of their critical solution temperatures have got a tendency to group themselves into clusters and that the finite value of the depolarisation of the opalescent light arises from the fact that the size of the clusters become comparable with the wavelength of light. Other experimental evidence such as the abnormal increase in the coefficient of viscosity and the thermal coefficient of magnetic and electric birefringence at the critical point support this point of view.

When a dust-free liquid is irradiated by a beam of monochromatic radiation and the light scattered by it is analysed by means of an ordinary spectrograph, a large part of the scattering which owes its origin to the fluctuations of optical density to have unaltered frequency. Examination of this "unmodified" scattering with the aid of a high-resolving power interferometer such as the Fabry-Perot Etalon however reveals it as split into three components one in the position of the original line and the other two appear displaced from it to the positions predicted by Brillouin's theory of light scattering (1922). The outer or Brillouin components owe their origin to pulsations of optical density taking place over an extended region in the fluid and travelling through the medium with the velocity of sound waves and thus giving rise to a Doppler effect. The appearance of a central component is attributed partly to the 'Q' branch of the orientation scattering and partly to the fluctuations of optical density of a quasi-static or static character. It is clear from the facts that an interferometric study of light scattering enables us to make a frequency analysis of the fluctuations of

optical density and to ascertain whether they occur with or without phase relationship within the fluid.

Such an investigation has not been carried out so far in the case of liquid mixtures and accordingly an interferometric study of the light scattered by liquid mixtures of both miscible and immiscible types was undertaken and the results are described in the present communication.

2. Experimental Details

The critical mixture chosen for the investigation consisted of (1) a polar and a non-polar liquid, viz., methyl alcohol and normal hexane and (2) two polar liquids, viz., *iso*-butyric acid and water. Two ordinary mixtures were also chosen. One was of two non-polar liquids namely benzene and *n*-heptane and the other of two polar liquids, namely ethyl alcohol and water which are miscible at all temperatures. Great care was taken to prepare all these mixtures perfectly dust-free and in the case of the critical mixtures with the correct critical composition, since the critical opalescence is most pronounced in such mixtures. The procedure adopted was as follows:—30% by weight of freshly distilled methyl alcohol was mixed with 70% by weight of distilled *n*-hexane and the mixture transferred into a flask having a capacity of about 400 c.c. This flask was connected to a Wood's tube of nearly 300 c.c. capacity and having a diameter of 3 cm. and length 20 cm. The flask containing the mixture was immersed in ice and the system evacuated and sealed off. The mixture was then distilled two or three times into the Wood's tube, each time washing the distillate back into the flask, the final distillation being carried out slowly till the whole of the mixture was almost completely distilled into the experimental tube. The same procedure was adopted for the *iso*-butyric acid-water mixture, the critical composition in this case being 50% by weight of each of the components. The two ordinary mixtures were also prepared in the same manner, their composition being 50% by volume of each of the components.

3. General Statement of Results

1. *Methyl Alcohol n-Hexane Mixture*.—The interference pattern obtained with a Fabry-Perot Etalon having 5 mm. separation for the 4810 A.U. radiation of the zinc-mercury amalgam arc, for this mixture at 30° C. is reproduced in Fig. (2) (d) [(the critical temperature being 29° C.). along with those of methyl alcohol and *n*-hexane (see Fig. (2) (b) and (c)]. Fig. 1 (a, b and c) gives the microphotometer curves for the same radiation. Both methyl alcohol and *n*-hexane have very intense and well-defined

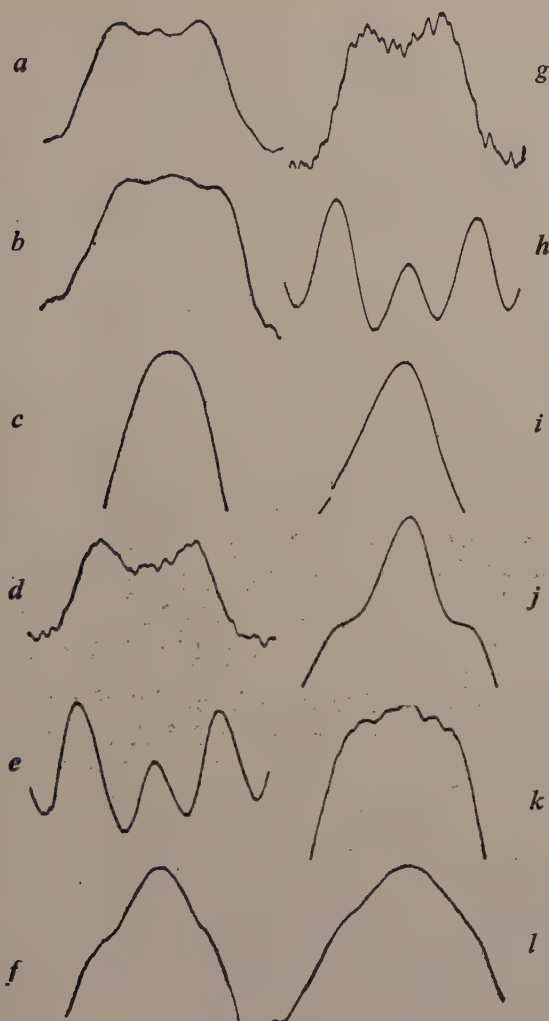


FIG. 1. Microphotometric Curves for Liquids

- | | |
|--|--|
| (a) Methyl alcohol | (g) <i>iso</i> -Butyric acid |
| (b) <i>n</i> -Hexane | (h) Water |
| (c) Methyl alcohol- <i>n</i> -Hexane mixture | (i) <i>iso</i> -Butyric acid-Water mixture |
| (d) Ethyl alcohol | (j) Benzene |
| (e) Water | (k) <i>n</i> -Heptane |
| (f) Ethyl alcohol-Water mixture | (l) Benzene- <i>n</i> -Heptane mixture |

Brillouin components, their wave number shift $\delta\nu$, respectively being 0.197 cm.^{-1} and 0.21 cm.^{-1} . The velocity of sound waves in these liquids is 1068 m./sec. for methyl alcohol and 1096 m./sec. for *n*-hexane. The

central component for methyl alcohol is very weak compared to the Brillouin components, while that for *n*-hexane has nearly the same intensity. In the mixture, however, we find the central component appearing with enormous intensity, but no trace of the Brillouin components is detected even in highly exposed plates.

2. *Iso-Butyric Acid-Water Mixture*.—The Fabry-Perot patterns for *iso*-butyric acid and water have already been investigated by Venkateswaran (1942) and his pictures and microphotometric curves for the same are reproduced respectively in Fig. 2 (*k*) and (*l*) and Fig. 1 (*g*) and (*h*). As can be easily seen from these photographs *iso*-butyric acid shows only an extremely weak central component and a strong continuum between the two intense Brillouin components. The spectral shift of the Brillouin components is 0.22 cm.^{-1} , the sound velocity being 1125 m./sec. Water on the other hand shows clearly all the three components the central component being slightly weak in comparison to the outer ones. The Brillouin shift for water is 0.28 cm.^{-1} , the velocity of sound being 1509 m./sec. The mixture at 30°C . [see Fig. 2 (*m*) and Fig. 1 (*i*)] however, shows no trace of the Brillouin components, as in the case of the mixture discussed above, in spite of the fact that the interference pattern is very intense.

3. *Benzene-n-Heptane Mixture*.—The interferometric patterns of benzene *n*-heptane and their mixture at 30°C . are respectively given in Fig. 2 (*p*), (*q*) and (*r*). Fig. 1 (*j*), (*k*) and (*l*) give the microphotometric curves for this mixture and its components. Benzene gives a very strong central component accompanied by two Brillouin components on either side of it, and of half its intensity; the spectral shift being 0.27 cm.^{-1} and the velocity of sound propagation 1275 m./sec.; *n*-heptane on the other hand, gives two strong and diffuse Brillouin components with a fairly sharp central component of slightly higher intensity. The spectral shift of these components is 0.23 cm.^{-1} and the velocity of sound propagation is 1161 m./sec. The mixture also unlike the above two critical mixtures shows all the three components. The mixture pattern has roughly the appearance of being a superposition of the patterns of the two component liquids. The velocity of sound propagation in this mixture is 1240 m./sec.

4. *Ethyl Alcohol-Water Mixture*.—The Fabry-Perot patterns obtained for the component liquids, viz., ethyl alcohol and water by Venkateswaran (1942) are reproduced in Fig. 2 (*g*) and (*h*) along with that of the mixture Fig. 2(*i*) obtained in the present investigation. Fig. 1 (*d*), (*e*) and (*f*) gives the microphotometric curves for the same. Here, as in the case of *iso*-butyric acid, ethyl alcohol gives slightly diffuse and very intense Brillouin components

accompanied by a sharp weak central component. As has been already mentioned in an earlier paragraph, water shows all the three components, the central component being slightly weaker than the outer ones. The mixture, on the other hand, shows a striking change. The central component exhibits a marked increase in intensity, the Brillouin components becoming relatively weaker than those of the component liquids. The velocity of sound propagation in water and ethyl alcohol is respectively 1509 m./sec. and 1130 m./sec. while that in the mixture is 1480 m./sec.

4. The Effect of Temperature

The two critical mixtures methyl alcohol-*n*-hexane and *iso*-butyric acid-water were also investigated at temperatures higher than the critical solution temperature. The interference patterns for methyl alcohol-*n*-hexane mixture at 40° C. and 50° C. are reproduced in Fig. 2 (e) and (f) and that of *iso*-butyric acid-water at 90° C. and 120° C. in Fig. 2 (n) and (o). The former shows no trace of the Brillouin components in spite of the fact that the mixture has been raised 21° C. above the critical temperature. The central component, however, becomes relatively sharper and weaker at higher temperatures. In *iso*-butyric acid-water mixture, on the other hand, the Brillouin components are clearly, though weakly seen at 90° C. The central component continues to be intense at all temperatures. The relative intensity of the shifted components to the central component becomes greater at 120° C.

Another fact of observation worthy to be recorded here is the relative intensity of the 5461 and 4358 A.U. radiations in the scattered spectrum. At the critical temperature, the green radiations are nearly as intense as the 4358 A.U. radiations; but as the temperature is raised by 20° C. or more, they become extremely weak, suggesting that the intensity of the opalescent light at the critical condition is proportional to λ^{-n} where n has a value much less than four [Andant (1924) and Rousset (1934)] and that at higher temperatures it tends to become proportional to λ^{-4} .

5. Discussion of the Results

The appearance of the Brillouin components in ordinary mixtures and the absence of the same in critical composition mixtures is very significant. One factor which might hinder the appearance of the Brillouin components is the abnormal increase in the coefficient of viscosity at the critical solution temperature reported by several authors such as Ostwald and Malss (1933) and Zofia Szafranska (1935). The effect of viscosity on the fine-structure components exhibited by pure liquids has been clearly brought out by

the studies of Venkateswaran (1942). Two important facts emerge out of his study on highly viscous liquids, viz., (1) that the Brillouin components are present though feebly in the case of liquids like glycerine and castor oil, even at room temperature, (2) that the ratio of the intensity of the Brillouin components to the central component increases rapidly with rise of temperature. In the case of glycerine at 110°C . the intensity of the Brillouin components is comparable to that of the central component.

Similar temperature investigations on methyl alcohol-*n*-hexane and *iso*-butyric acid-water mixture ought to reveal marked changes in the relative intensity of the Brillouin components to the central component. On the contrary, the present investigations show no trace of the Brillouin components in the case of methyl alcohol-*n*-hexane mixture even when its temperature is raised by 20°C . above its critical temperature and for *iso*-butyric acid by 45°C . In the latter, the Brillouin components appear weakly at 90°C . and when the temperature is raised to 120°C . they brighten up, but not to the extent expected for a range of 30°C . These results therefore suggest that changes of viscosity as such cannot account for all the observed facts.

We are therefore obliged to interpret the absence of Brillouin components as indicating that the critical mixtures are composed of molecular clusters of size comparable to the wave-length of the sound waves and which are randomly distributed thus preventing the free propagation of sound waves in these mixtures. The results of the study of the effect of temperature on the light-scattering by these two mixtures indicate that they remain as emulsoids for a wide range of temperature above their critical points about 20°C . for methyl alcohol-*n*-hexane mixture and 45°C . for *iso*-butyric acid-water mixture. This conclusion is in agreement with the observations of Krishnan (1935) who finds that the range over which the clusters are detectable in the case of critical composition mixtures is more than 30°C .

On the other hand the appearance of the Brillouin components with intensity comparable to that of the pure liquids in ordinary mixtures indicates that there is no likelihood of the existence of large molecular clusters in them. X-ray and other optical evidences lend support to this view. The enhanced intensity of the central component however suggests that the composition scattering forms an important part of the total scattering in these mixtures as well.

In conclusion, the author desires to express her grateful thanks to Prof. Sir C. V. Raman for his continued interest and encouragement in the course of the work. My thanks are also due to Dr. C. S. Venkateswaran for helpful suggestions.

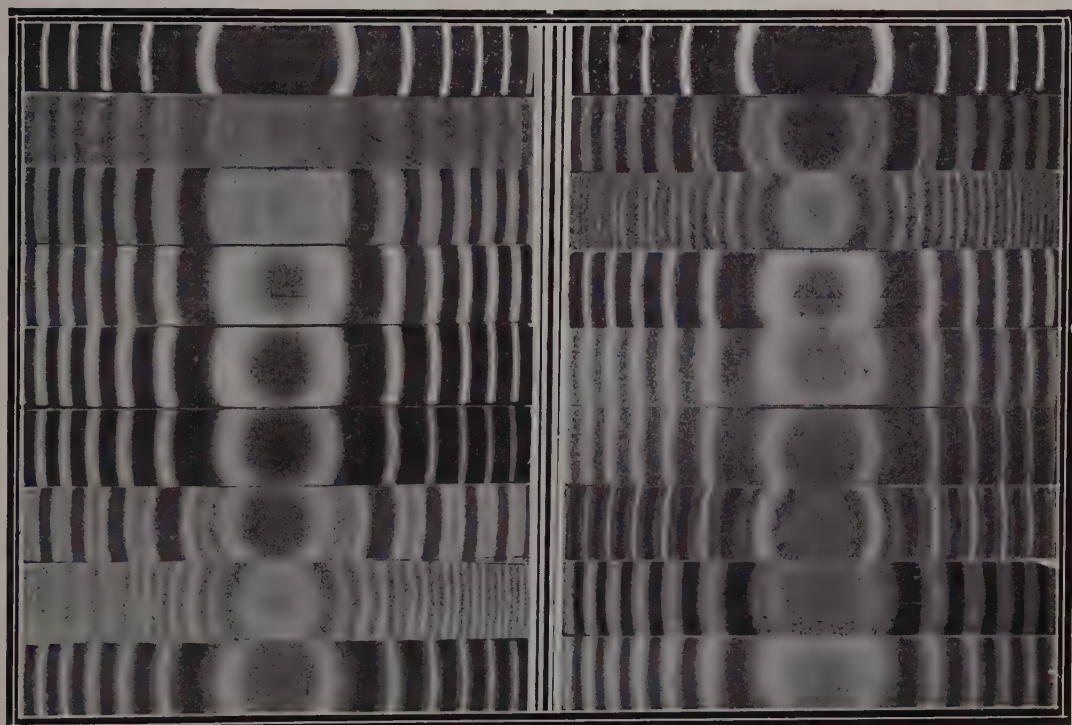


FIG. 2. Interferometric Patterns of Light Scattering in Liquids

- | | |
|---|---|
| (a) Direct Zn line (4810) | (j) Direct Zn line (4810) |
| (b) Methyl alcohol (30° C.) | (k) <i>iso</i> -Butyric acid (30° C.) |
| (c) <i>n</i> -Hexane (30° C.) | (l) Water (30° C.) (4078 Hg) |
| (d) Methyl alcohol- <i>n</i> -Hexane mixture (30° C.) | (m) <i>iso</i> -Butyric acid-Water mixture (30° C.) |
| (e) Do. (40° C.) | (n) Do. (90° C.) |
| (f) Do. (50° C.) | (o) Do. (120° C.) |
| (g) Ethyl alcohol (30° C.) | (p) Benzene (30° C.) |
| (h) Water (30° C.) (4078 Hg) | (q) <i>n</i> -Heptane (30° C.) |
| (i) Ethyl alcohol-Water mixture (30° C.) | (r) Benzene- <i>n</i> -Heptane mixture (30° C.) |

6. Summary

The fine structure of the opalescent light of two critical composition mixtures, viz., methyl alcohol-*n*-hexane and *iso*-butyric acid-water, has been studied at the critical solution temperature and higher temperatures. At the critical solution temperatures the Brillouin components are absent in either cases, while the central component is very intense. The former do not appear in the alcohol-hexane mixture even when its temperature was raised by 20° C. In the acid-water mixture, the shifted components are weakly present at 90° C. and found to increase in intensity at 120° C. In mixtures of miscible liquids namely benzene-*n*-heptane and ethyl-alcohol water also included in the present study, the Brillouin components are present prominently. The central component, however, shows enhanced intensity. These results indicate that a critical mixture at or above the critical solution temperature consists of molecular aggregates whose size is comparable to the wave-length of light and hence does not permit of the propagation of ordered sound wave trains of thermal origin. The significance of these results with reference to the Krishnan effect exhibited by binary liquid mixtures and the X-ray and other evidence is discussed.

REFERENCES

1. Andant, A. .. *Thesis*, Paris, 1924.
2. Brillouin, L. .. *Ann. de. Physique*, 1922, **12**, 88.
3. Einstein, A. .. *Ann. d. Phys.*, 1910, **33**, 1295.
4. Krishnan, R. S. .. *Proc. Ind. Acad. Sci. A*, 1935, **1**, 915.
5. Krishnamurti, P. .. *Ind. Jour. Phys.*, 1929, **3**, 331.
6. Ostwald, W., and Malss, A. *Koll. zeits.*, 1933, **63**, 61.
7. Ornstein, L. S., and Zernike *Proc. Amsterdam*, 1914, **17**, 79 ; 1916, **18**, 1520.
8. ————— .. *Phys. Zeits.*, 1918, **19**, 134 ; 1926, **27**, 761.
9. Raman, C. V., and Ramanathan, K. R. *Phil. Mag.*, 1923, **45**, 213.
10. Rousset, A. .. *Thesis*, Paris, 1934.
11. Smoluchowski, M. .. *Ann. d. Phys.*, 1908, **25**, 219.
12. Venkateswaran, C. S. .. *Proc. Ind. Acad. Sci., A*, 1942, **15**, 363.
13. Zofia Szafranska .. *Bull. Inter. Acad. Polonica. Class. Sci. Math. Nat.*, 1935 (A), **19**, 110.

ACTIVATION OF NITROGEN IN THE PRESENCE OF MERCURY

BY S. S. JOSHI AND A. PURUSHOTHAM

(From the Department of Chemistry, Benares Hindu University)

Received October 20, 1943

§1. APPRECIABLE divergence of opinion exists in regard to the effect of mercury on the life of active nitrogen. Strutt,¹ now Lord Rayleigh, observed: "Mercury gave an explosive compound, when its vapour was allowed to mix with active nitrogen." This was traced to the formation of mercury nitride. In a later paper² Rayleigh remarked: "No apparent effect is produced when the active gas is passed over clear cold metals or over a film of mercury held on copper; . . . if a small quantity of mercury is placed in the bottom of a fairly wide tube, and shaken while the active gas passes over it, all luminosity is extinguished and the mercury becomes foul. . . . If the shaking is discontinued, the glow again passes." It must be emphasised that this role of mercury in the above-mentioned and similar experiments of Rayleigh and others is fundamentally different from the finding that on extreme purification nitrogen fails to give the afterglow and that the introduction of but a small proportion of a foreign substance, *e.g.*, mercury vapour, restores it.² To quote Rayleigh²: "A drop of mercury was placed inside a tube so that by warming, it could be made to give off vapour, which mingled with the nitrogen stream, a marked restoration of the glow was observed, though it was less brilliant than that obtained with the best catalysts." On the other hand, Kichelu and Basu³ found: "For the measurement of pressure up to a certain stage, say 0.05 mm. Hg, a McLeod gauge was conveniently employed; but as the pressure of nitrogen became smaller any traces of mercury vapour had very destructive effect upon the life of active nitrogen, which quickly spent itself by acting upon mercury. . . . In the absence of liquid air it was found impossible to stop a slight diffusion of mercury vapour from the pump. . . . Even after these precautions, we did not find it possible to work with nitrogen below 0.02 mm." J. K. Robertson⁴ also observed that "the addition of mercury vapour at once destroys the glow." As a manometric liquid and for working the evacuating pumps, mercury is almost indispensable in any work on gas reactions. In view of this and especially the above marked differences of observation in the literature, it was of interest to investigate the action of active nitrogen on mercury over a wide range of conditions.

§2. Fig. 1 shows the essential parts of the apparatus employed. The cylindernitrogen containing 0.78% oxygen was passed through a train of bulbs filled with alkaline pyrogallol to remove oxygen; it was then stored for about 3 days before use in an aspirator in which was hung a muslin bag containing some considerable quantity of freshly cut yellow phosphorus.

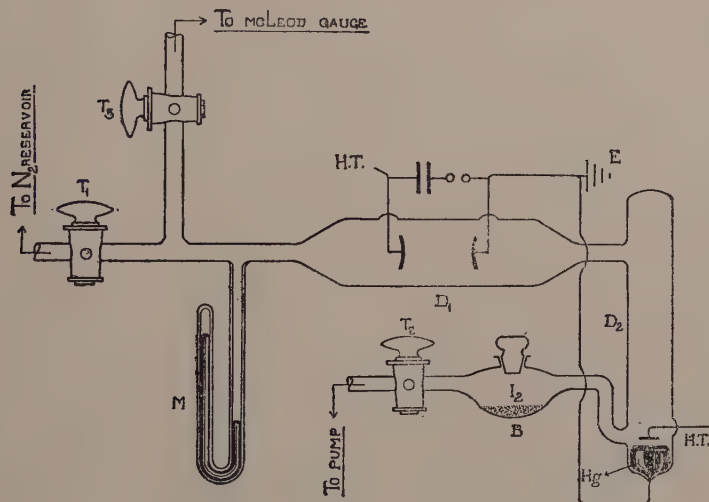


FIG. 1

No material differences were, however, observed so far as the nature of the results now to be reported are concerned, whether the gas was used after this purification or directly from the cylinder. By operating the suction pump and control of the stop-cocks the requisite pressure of nitrogen shown by the mercury manometer M was obtained; very low pressures were observed with a McLeod (not shown in the Fig.) connected at T_3 . The gas was activated by a condensed, spark-in-series discharge in the Crookes' type tube D_1 fitted with well-cleaned aluminium electrodes about 1 cm. in diameter and 1.5 cm. apart; the electrode on the suction side was earthed. One more discharge tube D_2 disposed vertically and in series with D_1 contained some pure mercury at the bottom, which was earthed; the other electrode was connected to the H.T. as in D_1 when required. D_2 was immersed in an oil-bath whose temperature could be varied in the range 30–300° C. A small amount of powdered iodine in B served as a sensitive detector of active nitrogen on account of the very characteristic luminescence which it excites when brought into contact with iodine. This served to detect active nitrogen which was too feeble for visual observation. The various parts of the apparatus

between T_1 and T_2 were connected by fused glass-joints and the system was repeatedly tested for vacuum on a Töpler, before final observations.

§3. In the first series of experiments nitrogen streamed at a pressure of 2–3 cm. Hg was activated in D_1 . The yellowish after-glow was well noticeable in D_2 on switching off the exciting voltage; with this on, and a well regulated suction, the glow was observable from D_2 upto T_2 . It was just tinged with the characteristic green luminescence of mercury when the gas was flowing through D_2 , which was kept at the ordinary temperature; was predominantly bluish-white due to iodine, in B; from T_2 to the exhaust end, the appearance was once more that of the normal after-glow of nitrogen. As the temperature of the bath was raised, the luminescence due to mercury predominated over the nitrogen glow in D_2 . Above 140°C ., mercury in D_2 boiled; this caused such an intensification of its luminescence that the after-glow of nitrogen was not perceptible in D_2 . It is considered that this marked increase in the intensity of the mercury luminescence is appreciably due to transfer of energy by collisions of the second type, between part of active nitrogen and mercury vapour in D_2 .⁶ That the glow of active nitrogen was but masked or rather overshadowed by the mercury luminescence was shown by the fact that the streaming gas produced the characteristic emission of iodine in B and that the familiar after-glow of nitrogen was distinctly perceptible beyond B, *i.e.*, between T_2 and the exhaust.

§4. Two series of experiments were next made in which nitrogen was activated by exciting the discharge tube D_2 containing mercury as the earthed electrode: with D_2 at $28\text{--}30^\circ\text{C}$., the iodine detector B and the apparatus beyond it showed a well-marked after-glow over a wide pressure range of the streaming gas. The same results were obtained in which instead of streaming, the apparatus between T_1 and T_2 was filled with nitrogen at a pressure varied in the range 1–2 cm. Hg, and D_2 was excited intermittently. After each cessation of the discharge, an after-glow marked enough to be identified with a direct vision hand-spectroscope, was seen in D_2 and extending appreciably on either side of it, for a time which increased on decreasing the gas pressure. With the above arrangement *i.e.*, with static nitrogen, on reducing the gas pressure the duration of the after-glow increased progressively; it was 5–6 minutes at about 0.0018 cm. Hg.

In the second series of experiments, the bath surrounding D_2 was heated to 160°C ., which produced a copious vaporisation of mercury. Nitrogen was then streamed at pressures varied from a few mm. to 2 cm. Hg. An *intense* after-glow was observed beyond D_2 upto T_2 , which was in marked contrast when the activated gas was allowed to flow into neutral mercury

vapour.²³ It may be added that mercury in D_2 was fouled and showed the formation of mercury nitride when tested in the usual way.

There is considerable evidence to show the formation, under electrical discharge in mercury vapour, of the excited and meta-stable states; their proportion would increase with temperature. It is to be anticipated therefore, that subjecting nitrogen to an electrical discharge under such conditions would favour, as is actually observed, the intensification of the after-glow by (i) the diminution of the probability of collisional de-activation and (ii) the direct activation of the gas by energy transfer from the excited and metastable atoms of mercury,⁶ and in collisions with the mercury ions moving under the action of the applied field.⁷

Summary

That active nitrogen is destroyed by contact with mercury is untenable as a general proposition. Their interaction produces the nitride and a variety of consequences depending upon the nature of conditions. When streamed into neutral mercury vapour, partial de-activation of active nitrogen and an excitation of the luminescence of mercury are the chief changes; the intensity of the latter increases with temperature and tends to overshadow that of nitrogen. When, however, the gas is excited with heated mercury as electrodes, the after-glow is markedly intense, which has been attributed to collisions with the excited and the metastable atoms of mercury, and its ions in the discharge space.

REFERENCES

1. Strutt .. *Proc. Roy. Soc.*, 1913, A 88, 539-49.
2. ——— .. *Ibid.*, 1915, A 91, 303-18.
3. Kichelu and Basu .. *Ind. Jour. Phys.*, 1929, 11, 161-73.
4. Robertson .. *Canadian Journ. Research*, 1932, 7, 444.
5. ——— .. *British Chem. Abst.*, 1933, p. 5.
6. Snaverly and Turner .. *Phys. Rev.*, 1931, 37, 1684; *British Chem. Abst.*, 1933, 200.
Kaplan .. *Ibid.*, 1931, 37, 226.
- Okubo and Hamada .. *Phil. Mag.*, 1928, 5, 372.
- Ruark .. *Ibid.*, 1928, 6, 335.
- McLennan, Rudy and Anderson .. *Nature*, 1928, 121, 537.
- Ruark, Foote, Rudnick and Chenault .. *J. Opt. Soc. Amer.*, 1927, 14, 17.
7. Joshi and Purushotham. *Nature*, 1942, 149, 250.

SOME ASPECTS OF THE BIOGENESIS OF ANTHOXANTHINS

BY P. SURYAPRAKASA RAO AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University, Waltair, now at Madras)

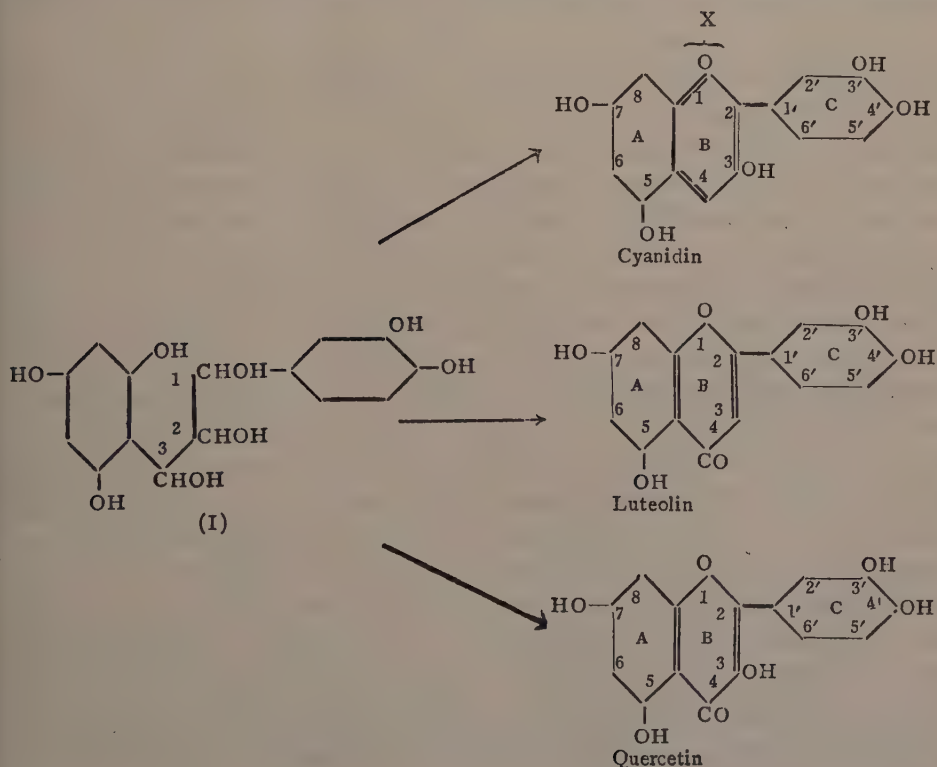
Received September 8, 1943

IN a recent publication was given a brief account of our knowledge about naturally occurring flavones and flavonols whose constitutions have so far been definitely known.¹ They were arranged into different groups depending upon the number and the orientation of the hydroxyl groups in the benzopyrone part of the molecules. Their occurrence and their characteristic properties were also recorded. From the data thus presented it seemed to be possible to obtain information regarding the manner of their evolution in the plant kingdom. Possibility of success in this venture appeared to be greater particularly in view of the valuable conclusions which Robinson and his collaborators have recently arrived at in regard to the biogenesis of the anthocyanins.²

Anthocyanins and anthoxanthins are two groups of closely related sap soluble pigments. They are built upon the same pattern having 15 carbon atoms and 3 rings. Even before their chemical constitutions were definitely known, biologists were impressed by their association and they considered that anthocyanins were generated from the anthoxanthins by a process of oxidation taking place in the plant.³ In support of this idea they could mention the comparatively later appearance of the bright red and blue colours due to anthocyanins and under conditions favourable to oxidation. When, as a result of the important work of Kostanecki, Perkin and others on the anthoxanthins and of Willstätter and his co-workers on anthocyanins, the chemistry of these two groups was made clear, the close chemical relation between them was established, but the anthocyanins represented a lower state of oxidation. Consequently the suggestion was made that anthocyanins were really products of reduction of flavones and flavonols, and no oxidation was involved.³ On either of these two ideas which mean sequential evolution of the pigments, a correlation could be expected between the individuals of the different groups occurring in the same parts of the plants. For example, pairs like pelargonidin and kempferol, cyanidin and quercetin, delphinidin and myricetin, should occur. In the cases examined in this connection this correlation could not be found. Further, the presence

of pelargonidin with myricetin, delphinidin with k  mpferol was not uncommon. In the few cases where correlation was found, cyanidin and quercetin were involved and this could be considered as incidental to their prolific occurrence in the plant kingdom.

The difficulties were satisfactorily explained by Robinson who developed the idea of parallel origin of these groups of compounds from a common source²; different degrees of oxidation are involved in the production of anthocyanins, flavones and flavonols. According to his scheme no correlation is required between the members of the different groups occurring together. On the supposition that anthocyanins and other related substances are built up from simple carbohydrates through a series of aldol condensations, the hypothetical intermediate (I) was suggested as the basis from which all these compounds are derived. The intermediate can be constructed from two hexose units and one triose, and is in the same state of oxidation as a carbohydrate. The central three-carbon fragment of (I) may be modified in several ways to give different end products. For example, oxidation at C₁ leads to the formation of cyanidin, at C₃ to the flavone, luteolin and at both C₂ and C₃ or at C₁ and C₃ to the formation of the flavonol quercetin.



During the past several years Robinson and his collaborators have been engaged in a survey of anthocyanins occurring in nature. Making use of a quick method of analysis requiring small quantities of plant material they have been able to study a very large number of samples and thus provide sufficient material for statistical analysis. It has been found by them that the basic structures concerned are remarkably small in number being pelargonidin, cyanidin and delphinidin. Only a few rare cases correspond to flavones, *i.e.*, they lack in a hydroxyl group in the 3 position; gesnerin and carajurin are the rare examples. Further from their data it could be concluded that cyanidin is the primary member of the anthocyanidins and the production of delphinidin (oxidation) and pelargonidin (reduction) involve one stage more in evolution. These are remarkable results and give great support in favour of structure (I) as the common precursor.

The study of the biogenesis of anthoxanthins is more difficult for several reasons. In contrast to the few basic types found in the anthocyanins the variations in flavones and flavonols are quite numerous. There are at least 18 flavonols and 12 flavones of established constitutions. Quick methods of analysis of plant materials for anthoxanthins have not yet been developed and hence it has not been possible to analyse such large number of samples as for anthocyanins. Further, whereas anthocyanins usually occur single and in some cases with one more as minor component, anthoxanthin mixtures are more frequently complex. Consequently the number of cases of complete analysis are limited and deductions cannot therefore be comprehensive. However, as stated at the beginning it seems to be possible to arrive at some conclusions based on the following considerations :—(1) since anthocyanins and anthoxanthins are closely related, the results obtained from the more comprehensive study of the former could be accepted as applicable for the latter also, (2) the association of compounds in the same part of a plant, in different parts of the same plant and in closely related plants could be utilised as evidence of biogenetic relationship. In regard to alkaloids and other well-defined groups of naturally occurring compounds it is quite well known that plants of the same family contain the same compounds or closely related compounds. The differences amongst them are only in finer details and not in fundamentals. The minor changes mainly due to oxidation, reduction and dehydration could be brought about differently or to different stages in different members of a group of plants, in different parts of the same plant or even in the subdivisions of the parts. But the main framework may be said to be evolved in the same way.

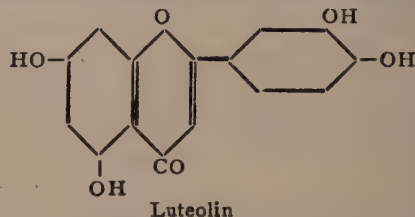
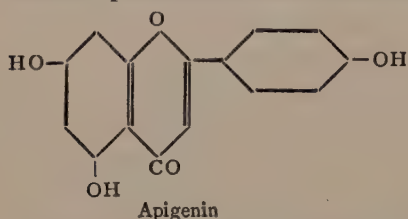
From consideration (1) given above, it follows that quercetin should be considered to be the simplest of the flavonols and luteolin the simplest of the

flavones and that the others require more stages for their evolution. This is also supported by the abundance of these two representatives in nature. Quercetin is the most frequently encountered anthoxanthin. Gisvold and Rogers⁴ give figures showing that out of 268 cases where anthoxanthins have been identified, 220 have the 3':4'-dihydroxy orientation in the substituted phenyl group. It could further be stated in general terms that as in the case of the anthocyanins, here also variations in the number of hydroxyl groups in the side phenyl nucleus is possible by the introduction of one stage more of oxidation or reduction, the positions 3' and 5' being involved. Support for the above statement is available from the association of compounds as they occur in nature and it is given later in this paper. The state of complete reduction leaving no hydroxyl in the side phenyl nucleus is common in the anthoxanthins and is a distinctive feature. But a more prominent characteristic of these compounds which does not find a parallel in the anthocyanins is the large variation in the state of oxidation of the benzene ring (A). In the latter group of pigments, two hydroxyls are invariably present in the 5:7-positions. Resoanthocyanins have not been found in nature. Carajurin represents an exceptionally rare case; but its occurrence indicates that the possibility of modification of ring (A) even in the anthocyanins cannot be excluded, though it may be uncommon. But in the anthoxanthins the variation in the number of hydroxyls is from 0 to 4. An explanation of this could probably be found in the marked difference in reactivity of the nuclear positions of anthoxanthins and anthocyanins after the structures have been formed from the common precursor, the modifications not taking place earlier. If quercetin and luteolin should be the simplest of the flavonols and flavones (containing hydroxyls in 5:7 positions) the biogenesis of the others should involve further stages of oxidation and reduction. How far this conclusion is justified and in what manner the variations arise can be indicated in a general way by a study of the pigment associations made below. Though in most of the cases considered the pigments occur as glycosides, only the aglycones are mentioned and used in the discussion. The nature of the sugars involved and the positions they occupy do not seem to be relevant for the present purpose. Similar considerations are applicable to the methyl ethers also. Further the list is not claimed to be comprehensive; typical cases alone are taken up and attention is particularly focussed on the evolution of special structures found only in the anthoxanthins and not in the anthocyanins.

I. Some associations of flavones and flavonols in which the side phenyl nucleus has different number of hydroxyl groups are given below. It could be noticed that compounds with one hydroxyl (4'-position) or three

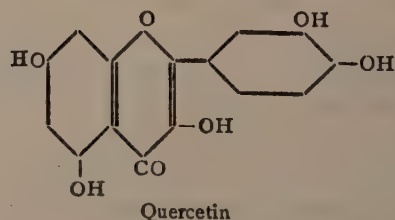
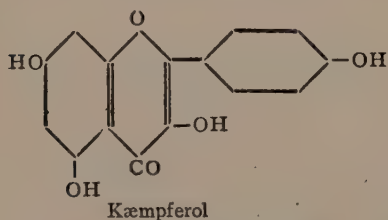
hydroxyls (3', 4' and 5') are accompanied by those with two hydroxyls (3' and 4'), indicating the evolution of the first two from the third. There seems to exist no definite cases where types with one and three hydroxyls in the side phenyl nucleus occur together, particularly to the exclusion of the 3':4' dihydroxy compounds.

(i) The combination of apigenin and luteolin is frequently met with in different parts of the same plant or in plants of allied species and varieties.



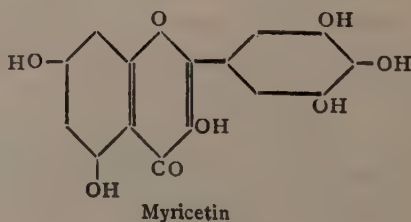
Apigenin occurs in the seeds of parsley, while in the stem and the leaves luteolin (as its monomethyl ether) is also present along with it.⁵ Both of them are found in the yellow variety of *Antirrhinum majus*⁶ and also in *Reseda luteola* (Weld.).⁷ The two varieties of *Chrysanthemum* yield the two related pigments; *C. indicum* contains luteolin and *C. leucanthemum* apigenin.⁸

(ii) Kämpferol is known to be found along with quercetin or its methyl ethers in several sources.

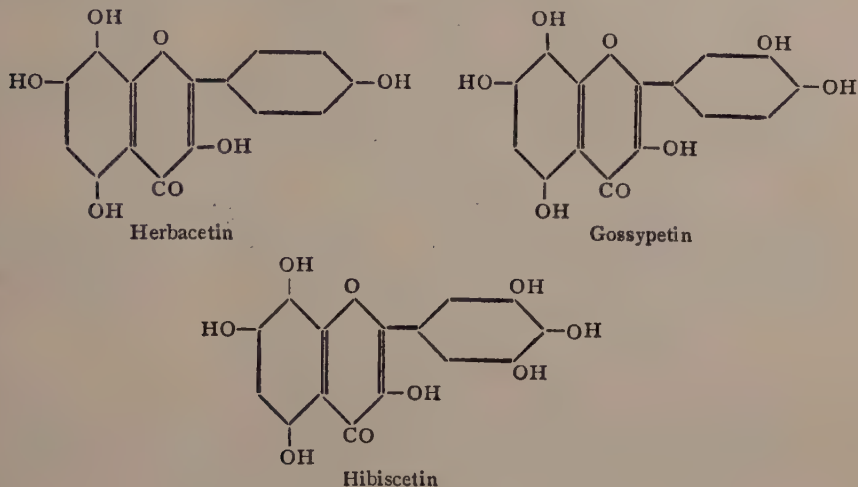


The stems of *Equisetum arvense* contain both these pigments, besides luteolin.¹⁰ In senna leaves kämpferol and isorhamnetin (3'-methyl quercetin) are present.⁹ The same combination occurs in the flowers of *Delphinium Zalil* (Asbarg).¹¹ Kämpferol and isorhamnetin along with kämpferol monomethyl ether are found in *Rhamnus catharticus*.⁹

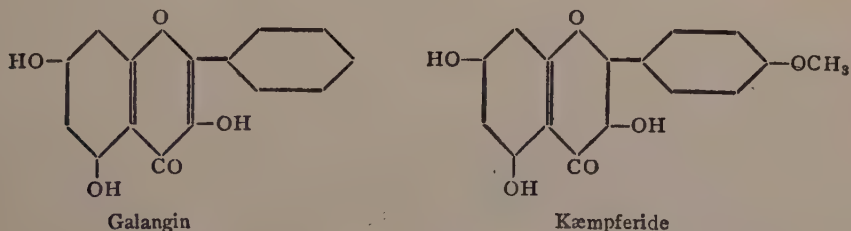
(iii) Quercetin and myricetin are both present in *Myrica nagi* and *Coriaria myrtifolia*.⁹



(iv) Indian cotton flowers (*Gossypium herbaceum* and *indicum*) contain gossypetin and herbacetin,¹² and in *Hibiscus sabdariffa* gossypetin and hibiscetin occur, the latter being the major component.¹³



(v) Galangin, its monomethyl ether and kæmpferide occur together in the galanga root.⁹ This example could be taken as indicating the sequence from the di- and monohydroxy side-phenyl nucleus to one devoid of hydroxyl groups.



II. In some plants quercetin occurs along with other compounds which contain one more hydroxyl group in ring (A).

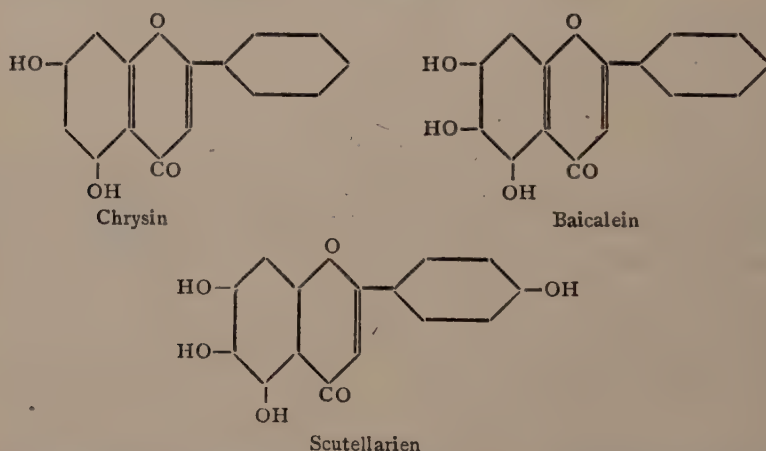
(i) The American cotton flowers, *G. hirsutum* contain as the sole component quercetin,¹⁴ whereas the Indian varieties *G. herbaceum* and *G. indicum* contain gossypetin and herbacetin besides quercetin, gossypetin being the major component.¹²

(ii) The flowers of two species of *Thespesia* have so far been examined. *T. lampas* was studied by Perkin and was found to contain quercetin.¹⁵ *T. populnea* has been shown by Rao and Reddy¹⁶ to contain herbacetin besides populnetin (a flavone whose constitution is not yet settled^{16a}).

From the above data, it seems to be reasonable to infer that quercetin is the primary stage, and gossypetin indicates a higher stage of evolution involving oxidation which leads to the formation of the hydroxyl group in position 8. Herbacetin is a subsequent stage of reduction resulting in the disappearance of the hydroxyl group in 3'-position in ring (C).

III. 5:6:7 Combination of three hydroxyl groups in ring (A) occurs fairly frequently. This also seems to be an evolution from the more fundamental 5:7-dihydroxy types involving oxidation.

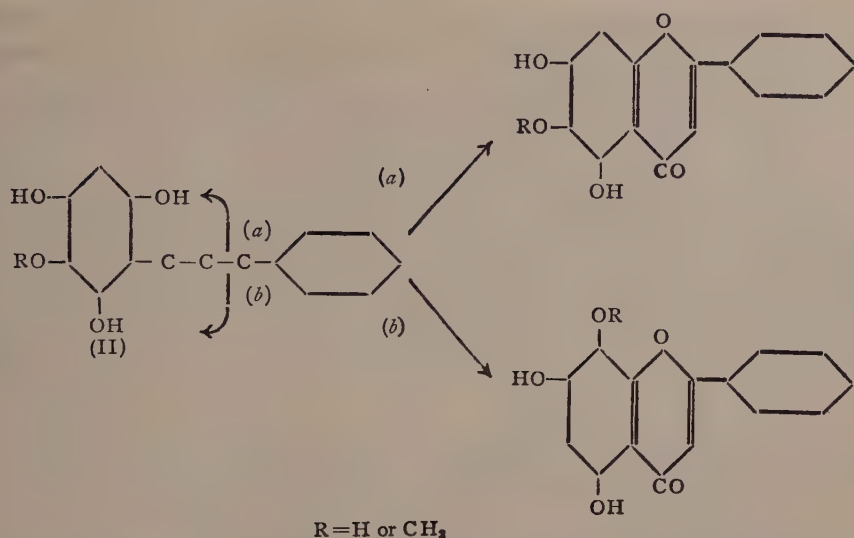
(i) The stem and root barks of *Oroxylum indicum* contain baicalein and its 6-methyl ether, oroxylin-A. Besides these two, the stem bark contains chrysin.¹⁷ Thus the relation between the 5:7-dihydroxy and the 5:6:7-trihydroxy compounds is indicated.



(ii) Regarding the existence of stages in the reduction of ring (C) the composition of the parts of different species of *Scutellaria* is useful. The leaves and flowers of *S. baicalensis* and *S. altissima* contain scutellarein¹⁸ whereas the roots of *S. baicalensis* contain baicalein.¹⁹

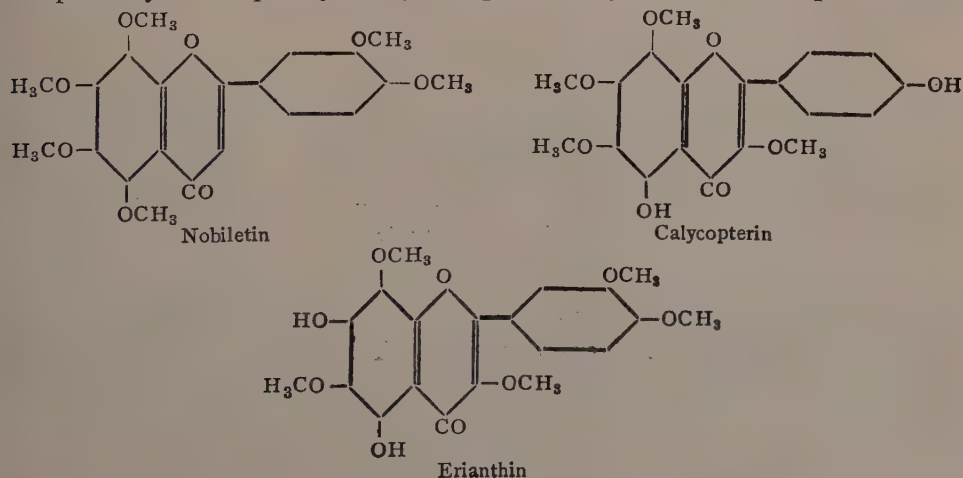
(iii) Another interesting point that should be noted here is that in the roots of *S. baicalensis*, wogonin, the 5:7:8 analogue of oroxylin-A is also found to be present¹⁹ and the ether group is in the 8-position. There are two ways of explaining this phenomenon:

(a) the 5:6:7 and the 5:7:8 combinations arise independently from the 5:7-dihydroxy compound by oxidation affecting position 6 or position 8 independently; (b) the oxidation takes place at some stage prior to the closure of the pyrone ring and the ring closure takes place in two different ways, one leading to the 5:6:7 and the other to the 5:7:8-configuration:



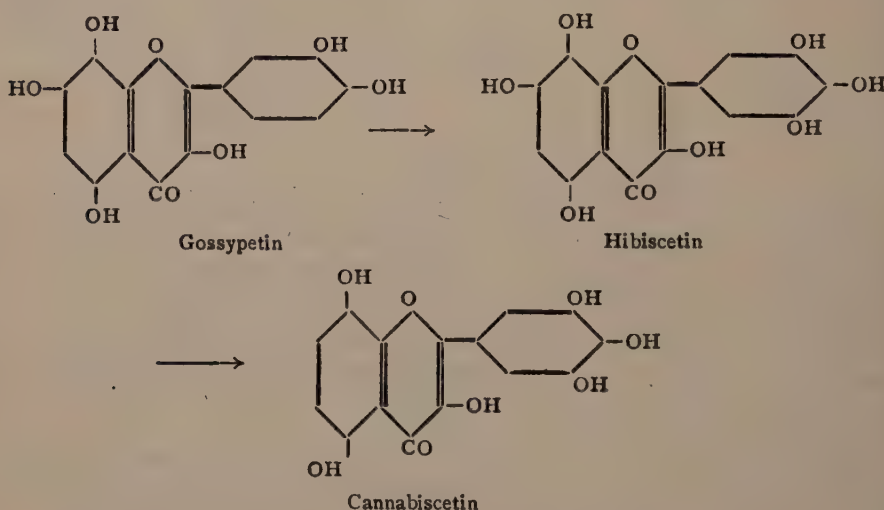
The existence of the second possibility is indicated by some laboratory experiments. But they are not numerous enough to be conclusive. The association of 5:6:7 and 5:7:8 types is found so far in one case only. It may not be, therefore, possible to say definitely which of the above two alternatives is more plausible. The first is probably more simple and also avoids certain other difficulties. It is, however, more definite that they are both derived from the 5:7-dihydroxy precursor.

IV. So far cases of one stage oxidation of the benzene ring (A) have been discussed. The idea could be extended to complete oxidation resulting in tetrahydroxy benzopyrone systems. Several of this type have been recently discovered. It is noteworthy that all these, nobiletin, calycopterin and erianthin are partially or completely methylated presumably in order to escape oxidation.



V. The following associations in closely related species indicate the existence of a stage of reduction of the hydroxyl group in position 7.

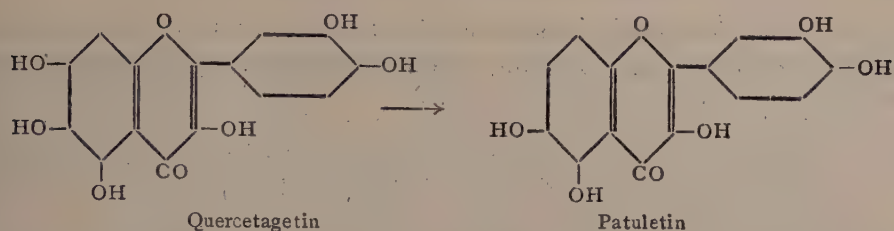
(i) *Hibiscus sabdariffa* contains hibiscetin as the main component and gossypetin and sabdaretin as the minor portion,¹³ whereas the closely related species, *H. cannabinus* contains cannabiscetin as the sole component.²⁰ The constitution of sabdaretin is not known yet and hence it is omitted from consideration. The relationship between the others can be expressed by the following formulæ and it seems to be reasonable to conclude that cannabiscetin is derived from hibiscetin by a stage involving reduction affecting position 7.



It may be mentioned here that in one experiment a small amount of cannabiscetin was found in *Hibiscus sabdariffa*; but it could not be isolated from other samples.

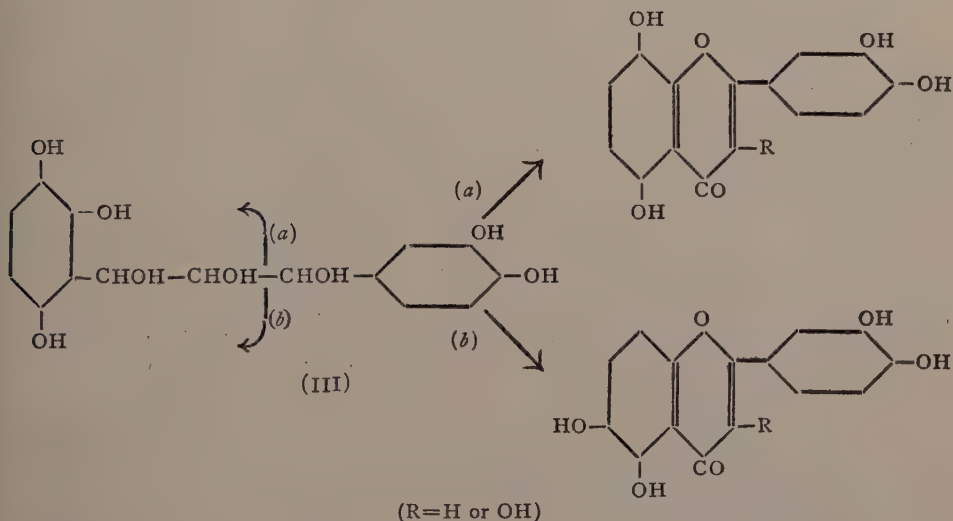
(ii) In this connection may be considered the components of the species of *Primula*. Primetin, 5:8-dihydroxy flavone, is obtained from the leaves of *P. modesta*.²¹ It is known that the flowers of *P. sinensis* contain pelargonidin or delphinidin glycosides depending on the variety.²² Obviously the compounds containing the 5:7 combination of hydroxyls are common in these plants and the evolution of the 5:8 type through the intermediate 5:7:8 is possible.

(iii) A very similar case arises in the two closely related flowers of the compositæ, *Tagetes erecta* and *T. patula*. The former contains quercetagetin and the latter patuletin in which the hydroxyl in the 7-position is missing.²³



The occurrence of the above-mentioned 5:8 and 5:6 combinations of hydroxyl groups which are not so common seems to be due to a stage involving reduction of 5:7:8 or 5:6:7 combinations whereby the 7-hydroxyl is lost. This process is obviously very rare but seems to exist definitely.

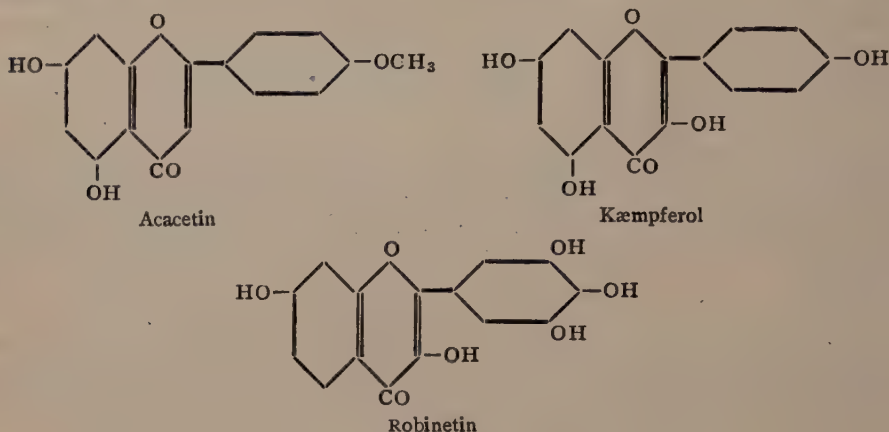
It could be suggested that the 5:6- and the 5:8-dihydroxy compounds are evolved from hydroxy quinol as shown below (III) instead of phloroglucinol present as part of the precursor (I).



But this idea is neither supported by the considerations of associations and plant relations discussed above nor by the occurrence of hydroxyquinol nucleus in other groups of compounds found in nature nor by the reactivity of this nucleus.

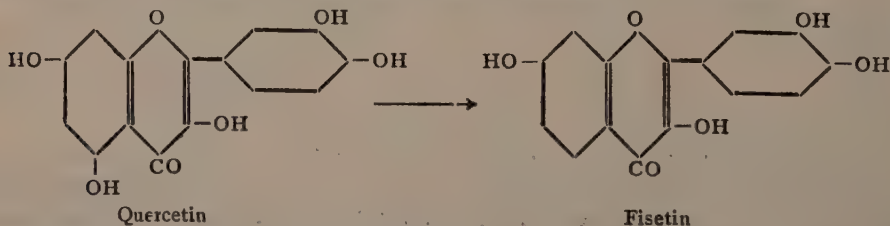
VI. There are two cases of compounds, fisetin and robinetin in which there is no hydroxyl group in the 5-position, only one being left in the 7th position. Are they evolved quite independently of the fundamental 5:7 compounds or are they derived from them? The second alternative is supported by the following considerations:—

(i) The leaves and bark of *Robinia pseudacacia* contain acacetin,²⁴ the flowers contain kæmpferol,²⁵ whereas the wood (dye wood) contains robinetin.²⁶



The association of 5:7 combinations with a compound containing only 7-hydroxyl group leads to the impression that it is derived from the fundamental dihydroxy compounds by a stage of reduction involving the hydroxyl in the 5-position. The possibility of oxidation or reduction in the side phenyl nucleus should be taken independently.

(ii) Other examples which support the above idea are obtained from "young fustic" and yellow cedar both of which are dye woods. The stem and branches of *Rhus cotinus* constituting "young fustic" contain fisetin, whereas the leaves of the plant (Venetian sumach) yield myricetin. In yellow cedar, fisetin is present in the stem and quercetin in the leaves.

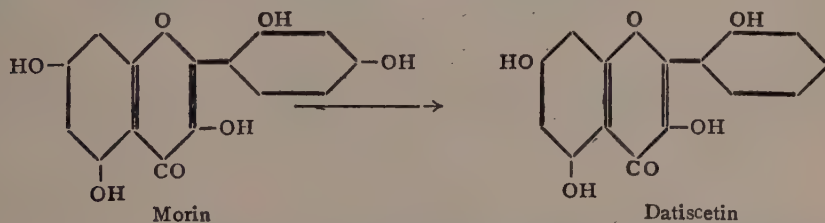


It is not unreasonable to consider fisetin as representing a later stage involving reduction resulting in the disappearance of the 5-hydroxyl found in quercetin. Myricetin, of course, is related to quercetin in a different way.

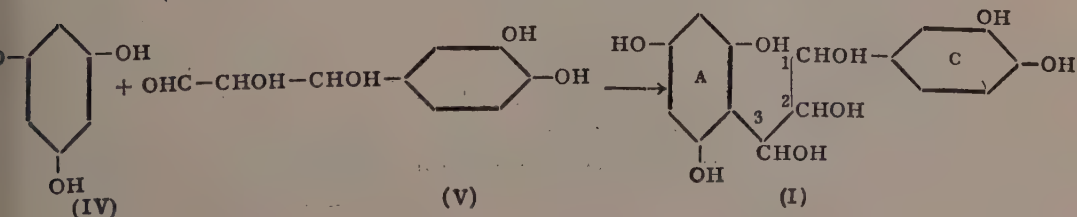
(iii) As a further example of this type may be mentioned pratol (7-hydroxy-4'-methoxy flavone) isolated by Power and Salway from the flowers of *Trifolium pratense*²⁷ and later by Rogerson from other species²⁸; it occurs in these along with quercetin and isorhamnetin.

From the data presented above the following conclusions could be arrived at. (1) The theory of Robinson regarding the origin of anthocyanins and anthoxanthins from a common precursor is supported. (2) The conclusion of Robinson and his collaborators regarding the stage of oxidation of ring (C) in anthocyanins could be applied to anthoxanthins also, *i.e.*, 3':4' combination of hydroxyls is the simplest and 3' and 3':4':5' combinations involve more stages. In the anthoxanthins complete reduction of the hydroxyls in ring (C) is represented by a large number of examples. (3) Superimposed on the changes brought about in ring (C), ring (A) is quite easily susceptible to changes involving oxidation and reduction of nuclear positions. 5:7 Combination of hydroxyl groups seems to be the primary state; 5:6:7- and 5:7:8-trihydroxybenzene structures involve a stage of oxidation and 5:6:7:8-tetrahydroxybenzene nucleus results from a further stage of the same nature. 5:8- and 5:6-dihydroxy types seem to result from trihydroxy types involving a stage of reduction leading to the disappearance of the 7-hydroxyl. Similar reduction seems to produce fisetin and robinetin in which the hydroxyl in the 5-position is lacking.

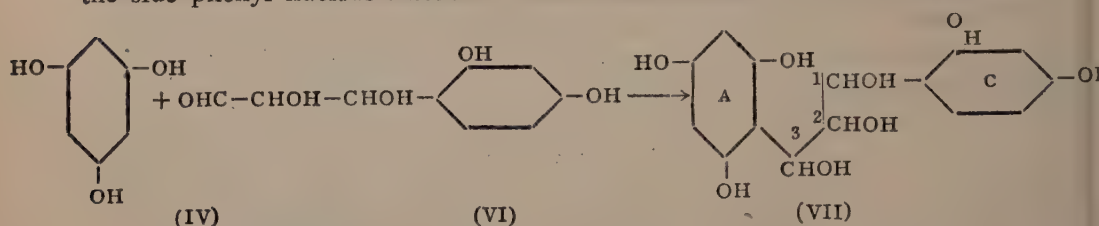
There is one more point that requires consideration. It relates to the occurrence of the two rare cases of flavonols morin and datiscetin. The former is found in "old fustic" (wood of *Chlorophora tinctoria*) and in jak wood whereas the latter is present in the leaves and roots of the bastard hemp. In the roots datiscetin is accompanied by galangin.²⁹



They have one hydroxyl group in the 2'-position. Obviously they belong to a rare type, but their occurrence may be taken as indicating the existence of a small variation from the fundamental precursor proposed by Robinson. This precursor is considered to be obtained from the union of two parts (IV) and (V), (IV) being phloroglucinol representing a hexose unit and (V) a nine carbon system derived from a hexose and a triose.



If the possibility of a variation in part (V) could be conceded as shown in (VI), then an alternative precursor (VII) having a resorcinol structure in the side phenyl nucleus instead of the catechol structure becomes available.



By the subsequent oxidation at C_1 and C_3 or at C_2 and C_3 morin could be obtained and from it involving a stage of reduction datiscetin could be evolved. But the occurrence of these types does not seem to be more common. The association of galangin with datiscetin is noteworthy. It could probably be derived from both catechol and resorcinol types of the side phenyl nucleus by complete reduction of the hydroxyl groups present in this part.

Summary

Based on the theory of Robinson *et al.* regarding the biogenesis of anthocyanins and on a detailed consideration of the occurrence of anthoxanthins (flavones and flavonols) in plants, a scheme of evolution of the various types of anthoxanthins is developed and discussed. Besides the existence of stages of oxidation and reduction of the side phenyl nucleus, similar modifications by oxidation and reduction of the benzopyrone part is involved. The possibility of a variation in ring (C) of the common precursor (I) as shown in structure (VII) leading to certain rare cases having hydroxyl groups in 2'- and 2':4'-positions is suggested.

REFERENCES

1. Rao and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1943, **17**, 119.
2. Robinson .. *Nature*, 1936, **137**, 172.
Robinson and .. *Phil. Trans. of Roy. Soc. of London*, 1939, **230 B**, 149.
collaborators
3. Onslow .. *The Anthocyanin Pigments of Plants*, Cambridge University Press, 1925.
4. Gisvold and Rogers .. *The Chemistry of Plant Constituents*, Mineapolis, 1938.
5. Von Gerichten .. *Ber.*, 1876, **9**, 1124.
6. Wheldale and Bassett .. *Biochem. J.*, 1913, **7**, 441.
Scott-Moncrieff .. *Ibid.*, 1930, **24**, 753.
7. Perkin and Horsefall .. *J.C.S.*, 1900, **77**, 1314.
Chevreul .. *Ann.*, **82**, 53.
8. Rao .. *Proc. Ind. Acad. Sci. (A)*, 1942, **15**, 123.

9. Perkin and Everest .. *The Natural Organic Colouring Matters*, 1918.
10. Nakamura and Hukuti .. *Br. Chem. Abs.*, 1941, A ii, 302.
11. Perkin and Pilgrim .. *J.C.S.*, 1898, 268.
12. Neelakantam, Rao .. *Proc. Ind. Acad. Sci. (A)*, 1935, 2, 490.
and Seshadri
- Neelakantam and .. *Ibid.*, 1936, 4, 54.
 Seshadri
13. Rao and Seshadri .. *Ibid.*, 1942, 15, 148.
14. Neelakantam, Rao .. *Ibid.*, 1935, 1, 887.
and Seshadri
15. Perkin .. *J.C.S.*, 1909, 95, 1859.
16. Rao and Reddy .. *Proc. Ind. Acad. Sci. (A)*, 1940, 12, 372.
- 16a. Neelakantam, Rao .. *Ibid.*, 1943, 17, 26.
and Seshadri
17. Bose and Bhattacharya .. *J.I.C.S.*, 1938, 15, 311.
18. Goldschmiedt ..
and Molisch .. *Monatsh*, 1901, 22, 679.
- Goldschmiedt ..
and Zerner .. *Ibid.*, 1910, 31, 439.
19. Shibata, Iwata and ..
Nakamura .. *J.C.S., Abs.*, 1923, A i, 592.
20. Neelakantam, Rao ..
and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1941, 14, 105.
21. Nagai and Hattori .. *Br. Chem. Abs.*, 1930, A, 784.
22. Scott-Moncrieff .. *J. Genet.*, 1936, 32, 117.
23. Rao and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1941, 14, 289 ; *Ibid.*, 1941, 14, 643.
24. Perkin .. *J.C.S.*, 1900, 423.
Hattori .. *Ibid., Abs.*, 1925, Ai, 1443.
25. Sando .. *J. Biol. Chem.*, 1932, 94, 675.
26. Schmid and Pietsch .. *Monatsh*, 1931, 57, 305.
27. Power and Salway .. *J.C.S.*, 1910, 97, 231.
28. Rogerson .. *J.C.S.*, 1910, 97, 1006.
29. Kalff and Robinson .. *Ibid.*, 1925, 1968.

THE VIBRATION SPECTRUM OF A CRYSTAL LATTICE

BY SIR C. V. RAMAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received August 26, 1943

1. Introduction

It is a fundamental problem in the physics of the solid state to determine the possible modes and frequencies of vibration of the atomic nuclei in a crystal about their positions of equilibrium. The importance of the problem will be evident when we recollect that there is scarcely any physical property of a solid which is not influenced in greater or less measure by the thermal agitation of the atoms, and that the existence of atomic vibrations (excited thermally or otherwise) comes into evidence in a variety of phenomena exhibited by crystals. We may, in particular, mention various optical effects observed with crystals, *e.g.*, the scattering of light with altered frequency, luminescence and absorption spectra at low temperatures, which not only render the existence of atomic vibrations in them obvious, but also enable us to make precise determinations of their vibration frequencies, and even infer their geometric characters.

An appropriate starting point for the inquiry is furnished by the well-known result in analytical mechanics that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. In each such mode, the particles of the system execute harmonic vibrations with a common frequency characteristic of the mode, and all pass simultaneously through their positions of equilibrium at some particular phase of the vibration. The question arises for investigation, does the structure of a crystal possess any normal modes of vibration as thus defined, and if so, what are their frequencies? In seeking an answer to this question, it is obviously not permissible to make in advance any arbitrary postulate regarding the nature of the normal vibrations, since this is itself the subject-matter of the investigation. Further, it is essential that we assume the most general type of interaction possible between the atoms in the crystal which is consistent with its known structure and symmetry properties. Indeed, in an investigation intended to

deduce results of general application, it is evidently undesirable to make any special postulates regarding the interatomic forces, *viz.*, that they are only operative as between contiguous atoms or that they are in the nature of central forces whose magnitude varies as some power of the distance. The introduction of arbitrary postulates and assumptions has indeed, as will be shown in this paper, led to misleading results in the past history of the subject.

2. The Lagrangian Equations of Motion

We denote the displacements of a chosen atom in a particular cell of the crystal structure from its position of equilibrium by the symbols q_{xrs} , q_{yrs} , q_{zrs} , these being parallel respectively to the three mutually perpendicular co-ordinate-axes x , y and z . Here r is an index number indicating a particular atom amongst the p atoms in the cell of the crystal structure, while s is an index number indicating the particular cell in which the atom is located. The symbols $q_{x\rho\sigma}$, $q_{y\rho\sigma}$, $q_{z\rho\sigma}$ have a similar significance, except that ρ and σ which are the atom and cell indices respectively are regarded as unspecified. The masses of the atoms are written as m_r or m_p .

The kinetic energy T of the vibrations of the crystal is accordingly given by the summation over all possible values of ρ and σ of the expression

$$\frac{1}{2} m_p [\dot{q}_{x\rho\sigma}^2 + \dot{q}_{y\rho\sigma}^2 + \dot{q}_{z\rho\sigma}^2]. \quad (1)$$

The potential energy V of the displacements of the atoms from their positions of equilibrium is given by the summation of all the terms derived from the expression

$$\frac{1}{2} K_{rs}^{\nu\rho\sigma} \cdot q_{rs} \cdot q_{y\rho\sigma} \quad (2)$$

by making r , s , ρ , σ run over all the possible values, as also by interchanging x , y and z . The dependence of the force-constants jointly on x , r , s and y , ρ , σ is indicated by the indices attached to them. It is evident that

$$K_{rs}^{\nu\rho\sigma} = K_{yrs}^{\sigma\rho\nu}. \quad (3)$$

Hence, since each distinct pair of co-ordinates appears twice over in the summation, we may replace the factor $\frac{1}{2}$ by 1 in (2), it being understood that they are written together only once. The factor $\frac{1}{2}$ is however retained for the terms which appear as the squares of the displacements.

The equation of motion which must be satisfied by any particular co-ordinate, *e.g.*, q_{xrs} is

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_{xrs}} \right) + \left(\frac{\partial V}{\partial q_{xrs}} \right) = 0. \quad (4)$$

If we assume that the vibration under consideration is a normal mode for the crystal, the displacement-components of all the atoms must be of the form $q \sin \omega t$ where the q 's are real quantities depending on the atom chosen

and the direction of its displacement, while ω is the same for all atoms in the crystal. On this basis, the equation for q_{xrs} becomes

$$(m_r \omega^2 - K_{rs}^{rrs}) q_{rs} = \sum_{y\rho\sigma} K_{rs}^{y\rho\sigma} \cdot q_{y\rho\sigma}. \quad (5)$$

The summation indicated on the right-hand side of (5) is to be understood as including the contributions due to all the displacement-components of all the atoms in the crystal with the single exception of the displacement q_{xrs} under consideration which appears on the left-hand side of the equation. There would, of course, be a whole series of equations of this type for the x , y and z displacements of every atom in the crystal, and it is necessary that all these equations are simultaneously satisfied for the given value of ω , for the vibration under consideration to possess the characters of a normal mode.

3. The Solution of the Equations

The clue to the discovery of the normal modes of vibration is furnished by the basic principle of crystal architecture which may be stated as follows: *A crystal consists of sets of equivalent atoms ordered in such manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set.* From this it follows that the force-constant which connects the displacements of any pair of atoms in the crystal is the same as that which connects the displacements of any other pair of atoms, provided that the two pairs of atoms can be simultaneously brought into coincidence by simple translations of the crystal lattice parallel to its axes.

Consider now the equation of motion analogous to (5) for the r th atom in a different cell, say s' . In writing it down, it is convenient to choose a running cell-index σ' different from the σ appearing in (5), but so related to it that the translations of the crystal lattice which would bring s' into coincidence with s would also bring σ' into coincidence with σ . We have then

$$(m_r \omega^2 - K_{rs'}^{rrs'}) q_{rs'} = \sum_{y\rho\sigma'} K_{rs'}^{y\rho\sigma'} \cdot q_{y\rho\sigma'}. \quad (6)$$

Now the relation between s , σ and s' , σ' assumed above, taken in conjunction with the physical structure of the crystal, gives us at once the relations

$$K_{rs}^{rrs} = K_{rs'}^{rrs'} \quad (7)$$

$$K_{rs}^{y\rho\sigma} = K_{rs'}^{y\rho\sigma'} \quad (8)$$

between the force-constants appearing in (5) and (6). This identity of the force-constants appearing on both sides of the equations of motion of equivalent atoms suggests that their displacements in a normal mode of vibration

are also related to each other in a simple way. Algebraically, it is evident that if there exists between them a general relationship of the form

$$\frac{q_{xrs}}{q_{xrs'}} = \frac{q_{yp\sigma}}{q_{yp\sigma'}}, \quad (9)$$

it follows therefrom that when equation (5) is satisfied, equation (6) will also simultaneously be satisfied, and indeed also the similar equations for *all* the equivalent atoms of index *r* in the crystal. Further, if the general relations indicated in (9) subsist, they are sufficient to ensure that when the equations of motion of an atom of *any* chosen index number is a particular cell are satisfied, the equations of all the other equivalent atoms of the same index number in every other cell of the crystal lattice are also simultaneously satisfied; the latter is a necessary condition for the vibration to be a normal mode.

4. Nature of the Normal Modes

We shall now consider more closely the significance of the relations stated in (9). They may be written in the form

$$\frac{q_{yp\sigma}}{q_{xrs}} = \frac{q_{yp\sigma'}}{q_{xrs'}}. \quad (10)$$

Stated in words, the meaning of (10) is that the vibrations of the equivalent atoms in the crystal are quantitatively related to the vibrations of the other atoms forming their respective environments in an identical fashion. *Prima facie*, this is what we should expect, since equivalence of geometric position in the crystalline array of atoms necessarily involves an equivalence in the strength of the forces holding the atoms together as indicated in equations (7) and (8), and hence should result also in equivalence in respect of dynamic behaviour in a normal vibration. To make the meaning of such equivalence clearer, we may return to equation (9) and take a case in which the cells *s* and *s'* occupy contiguous positions along one of the axes of the Bravais lattice. It follows that *σ* and *σ'* would similarly occupy contiguous positions along a parallel axis. Equation (9) thus signifies that the ratio of the corresponding displacements of *any pair* of contiguous equivalent atoms in the crystal lattice is a constant characteristic of the particular axis and of the particular normal mode under consideration.

We may apply the same arguments to cells contiguous to each other respectively along the second and third axes of the Bravais lattice. The three characteristic constants thus obtained need not necessarily be the same, and we therefore devote them by *α*, *β*, *γ* respectively. Since the atomic displacements are real quantities and their phases in a normal mode are all either the same or opposite, the constant ratios *α*, *β*, *γ* must be assumed to

be *real* quantities which may be either positive or negative. If, starting from a particular cell, we move out to another which is reached by u, v, w primitive translations in the positive directions along the three axes of the Bravais lattice, the amplitude of the vibration of corresponding atoms would be altered in the ratio $\alpha^u \beta^v \gamma^w$, while if we similarly proceed in the negative direction, we would reach a cell in which the amplitudes are altered in the ratio $\alpha^{-u} \beta^{-v} \gamma^{-w}$. Hence, if α or β or γ is numerically different from unity, we may, by proceeding sufficiently far in one direction or another from an arbitrarily chosen cell where the amplitude is small, reach cells where the amplitudes are larger than any assigned limit. Hence, the initial postulate that the vibration amplitudes are everywhere small can only be sustained if the constants α, β, γ are numerically equal to unity, and are either positive or negative. We thus obtain the result

$$\alpha = \pm 1, \beta = \pm 1, \gamma = \pm 1. \quad (11)$$

The possible choices from amongst the alternative signs in the three equations (11) are evidently independent. We have therefore *eight* possible cases, all of which are covered by the following description: *Equivalent atoms in the crystal have all the same amplitude of vibration, their phases being either the same or else opposite in successive cells of the lattice along each of its three axes.* We may also describe the position as follows: *The atomic vibrations repeat themselves exactly in a space-pattern of which the unit has twice the dimensions in each direction and therefore eight times the volume of a unit cell of the crystal lattice.* We may interpret these statements physically by considering the well-known result of coupling two exactly similar oscillators to each other, namely the appearance of two types of vibration in which the oscillators have the same phase and the opposite phases respectively. In other words, the dynamic behaviour of a crystal is a three-dimensional analogue of the case of two coupled oscillators.

5. Enumeration and Description of the Modes

We have now to consider the question whether the relations stated above in equation (11) uniquely determine all the possible normal modes of the atomic vibrations in a crystal. The readiest way in which we can satisfy ourselves that this is the case is by considering the question from a physical point of view. The significance of equation (11) can be stated in the following manner: *In every normal mode of vibration, the energy of the vibration is the same for every individual cell of the crystal lattice, while the amplitudes have either the same signs or else have alternately opposite signs in the successive cells.* The two parts of the proposition are complementary and taken together characterise the normal modes completely. It is easy

to see that no vibration in which either or both of these characters is departed from can be a normal mode. If, for example, the energy of the vibration were to vary from cell to cell, it would be obviously not possible for such a state of affairs to continue permanently in a homogeneous structure. Energy would be progressively transferred from the cells having the greater energy to those having less, and the nearer the cells are to each other, the more rapidly would this process occur. A normal vibration is, by definition, perfectly time-periodic and hence, the equality of the energy of vibrations in the different cells is a necessary feature of it, and this in turn is only possible if equivalent atoms have the same amplitude of vibration. It only remains therefore to consider the question of the phases. Here, again, the definition of a normal mode allows only two alternatives, namely a positive or a negative amplitude. The effect of reversing the phase of the vibration of the atom without altering its amplitude is to change the sign of the term contributed by it to the equation of motion of every atom in the crystal, leaving its magnitude unaltered. From this, it follows that equations (5) and (6) cannot be simultaneously satisfied unless all the corresponding atomic displacements have the same signs in the two equations or alternatively have all the opposite signs. These requirements are satisfied by the eight dispositions indicated by equations (11), but not by any other conceivable arrangement of positive and negative amplitudes of equal magnitude over the cells of the lattice.

The relations stated in (11) enable us to reduce the number of independent equations of the type (5) which have to be solved from an infinite set to just $3p$ equations for each of the eight distinct cases arising therefrom. The constants appearing on the left-hand side are, of course, different in each of the $3p$ equations of each set. The terms appearing on the right-hand side of each equation may be grouped into sets in which each of the $(3p-1)$ co-ordinates involved appears multiplied by what is technically an infinite series. Physical considerations, however, indicate that these series should be convergent and summable. Each of them may therefore be replaced by a single new constant. In other words, for each of the eight distinct cases arising from (8), we may frame a set of $3p$ equations connecting the $3p$ co-ordinates, the constants appearing in them having new values. The solution of the sets of equations thus obtained would enable both the normal modes (*viz.*, the ratios of the atomic displacements) and the normal frequencies to be evaluated.

It thus becomes evident that the number of normal modes and normal frequencies for each of the eight cases arising from (8) is $3p$. In other words, we have $24p$ normal modes and normal frequencies, which is the

same number as the degrees of freedom of the $8p$ atoms whose vibrations form the repeating pattern in space. It should, however, be remembered that we have started from the assumption that the crystal as a whole is at rest. Its centre of gravity must therefore remain fixed, and this gives three conditions of constraint which would reduce the number of solutions by 3. Thus in all, we have only $(24p - 3)$ normal modes and frequencies of vibration. The individual cell of the crystal lattice is the unit of the repeating pattern in space for $(3p - 3)$ of these modes, the atoms in the cell vibrating against each other. The repeating pattern in space for the remaining $21p$ normal modes is the super-cell already considered which has twice the dimensions and eight times the volume of a unit cell of the lattice.

It is possible to give simple geometric descriptions of the eight different types of normal modes arising from equation (11). The modes described by $\alpha = 1, \beta = 1, \gamma = 1$ may be pictured as oscillations with respect of each other of the p interpenetrating Bravais lattices of atoms of which the crystal is built up. There would be $(3p - 3)$ such modes, while the other 3 degrees of freedom of these lattices may be identified as simple translations of the entire crystal which we have already excluded from the scheme. The remaining $21p$ normal modes may be pictured as oscillations relative to each other of the alternate planes of equivalent atoms in the crystal. If for example, $\alpha = 1, \beta = 1$ and $\gamma = -1$, the alternate planes of the atoms containing the α and β axes and intersecting the γ axis would oscillate against each other. If $\alpha = 1, \beta = -1, \gamma = -1$, the alternate planes of atoms passing through the α axis and cutting both the β and γ axes would oscillate against each other. If α, β, γ are all negative, the oscillating planes of atoms would intersect all the three axes at the appropriate angles. In the case of a cubic crystal, for example, the oscillating planes of atoms would be those respectively parallel to the cubic, dodecahedral and octahedral faces of the crystal.

6. *Nature of the Atomic Frequency Spectrum*

The result which emerges from the foregoing discussion is that the *vibration spectrum of the crystal consists of a set of discrete monochromatic frequencies which may be described as arising from the vibrations against each other of the atoms located in the units of an 8-cell super-lattice*. In deducing this result, we have regarded the crystal as a three-dimensionally periodic structure infinitely extended in space, and ignored the existence of any external boundary. This procedure appears justified. For, in the equations of motion of an atom, the terms contributed by the other atoms in the crystal must necessarily be assumed to form a convergent

series, in other words, their influence on its motion reaches a limiting value when the size of the crystal is increased indefinitely. Hence, the presence or absence of an external boundary can make no sensible difference to the modes of the atomic vibrations in the interior of the crystal.

It may be remarked also that the number of discrete frequencies observable would be very considerably diminished if the crystal belongs to a class exhibiting a high type of symmetry. For, in such a case, several of the modes of vibration reckoned as distinct in the preceding enumeration would possess identical frequencies. Taking for instance a crystal of the cubic system, we recognize that the symmetry of the crystal would result in the eight distinct sets of frequencies indicated by equation (8) being in effect reduced to four. In one set of normal modes, all equivalent atoms in the crystal move in the same phase: in three sets of normal modes, the equivalent atoms so moving lie in planes parallel to one or another of the cube faces and the corresponding frequencies would therefore be the same; in three others again, planes of atoms parallel to the dodecahedral faces move in the same phase, and the corresponding frequencies will therefore be identical: in the eighth set, the planes of atoms moving in the same phase are parallel to the octahedral faces. The total number of distinct frequencies possible is thus reduced from $(24p - 3)$ to $(12p - 3)$. A further reduction will arise if the directions of movement of the atoms in normal modes reckoned as distinct in this enumeration are actually equivalent. For instance, the existence of a normal mode in which all the equivalent atoms oscillate parallel to one of the cube axes necessarily involves the possibility of two others having the same frequency. In these and other ways, a very considerable reduction in the number of distinct frequencies and consequent simplification of the vibration spectrum would result.

7. *Elastic Vibrations of the Crystal Lattice*

As already remarked, the $24p$ degrees of freedom of the atoms contained in the cells of the super-lattice gives us only $(24p - 3)$ normal modes of atomic vibration. The 3 degrees of freedom of translation of the super-cell left over in this enumeration must therefore be assigned to modes of vibration of a different nature. The natural assumption to make is that they represent the lower frequencies of vibration coming under the general description of elastic vibrations of the crystal lattice. On this basis, the elastic vibrations represent only one-eighth of the total number of degrees of freedom in the case of crystals consisting of a single Bravais lattice, one-sixteenth of the number when there are two interpenetrating Bravais lattices, and a still smaller proportion when there are three, four or

more atoms in the unit cell, finally becoming a negligible fraction of the whole in crystals of even moderately complex structure.

According to the classical theory of elasticity, waves of any frequency and of corresponding wave-length are possible within an infinitely extended solid, but specific modes of elastic vibration can only exist in a solid of finite extension, its shape and dimensions determining the modes as well as their frequencies. As we have seen, however, an atomistic approach gives a wholly different result, *viz.*, that the normal modes and frequencies are determined by the internal structure of the crystal, the form and dimensions of the external boundary being irrelevant. The apparent contradiction between these conclusions disappears when we notice that the classical theory of elasticity describes the low-frequency region of the vibration spectrum, while the atomistic theory describes the high-frequency end. The two types of vibration differ in important respects. In the atomic vibrations properly so called, the absolute and relative atomic displacements are throughout of comparable magnitude, while in the elastic vibrations, the translatory movements of the lattice cells are greater than the relative atomic displacements approximately in the ratio of the wave-length to the cell dimensions. While the two types of vibration may possibly tend to resemble each other in a transitional range, we are not justified in extrapolating either theory into the region of frequency in which it is wholly inapplicable.

The inappropriateness of the elastic solid theory in considering the high-frequency vibrations of a crystal lattice needs to be particularly emphasised. The theory is based on the idea that the material is a continuum having a uniform density and elasticity, whereas in reality, the crystal has a discrete atomistic structure. X-ray investigations show that the electron-density in a crystal is not uniform but is a triply-periodic function of position. The Fourier components of the electron density have noteworthy amplitudes, but they fall off with increasing order rapidly. The discontinuity of crystal structure is even more striking when we consider the mass-distribution. This is concentrated at the individual lattice points occupied by the atomic nuclei, and a Fourier analysis of the density distribution would therefore give component amplitudes which do not diminish with the order and each of which would by itself be greater than the average density of the crystal (by a factor of two in the case of a single set of atomic planes). This is a state of affairs very remote indeed from the uniform mass-density and elasticity assumed in the classical theory. Hence, only when the elastic wave-lengths are large compared with the crystal spacings could we expect a concordance between the facts and the results of that theory. For smaller wave-lengths and higher frequencies, the theory must fail, as is evident

when we consider the behaviour of elastic waves in a medium exhibiting very pronounced stratifications of mass density or elasticity. If the Fourier components of space-variation of density were *small*, we would have selective reflections of the elastic waves analogous to the familiar optical or X-ray reflections by stratified media. The *large* amplitude of the Fourier components of mass-density however alters the situation radically, and it is readily shown that *the bands of selective reflection of the elastic waves would broaden so greatly as to result in a complete cut-off of the high-frequency region of the spectrum*.^{*} In the region of high frequencies, therefore, the ideas of the elastic solid theory are wholly irrelevant and inapplicable, and an atomistic approach to the theory becomes absolutely necessary.

One might, on the other hand, be tempted to carry over the atomistic approach which proves successful in the high-frequency region towards lower frequencies. To do this, one may assume that modes of vibration exist in which groups of atoms, as for example the super-cells considered earlier in the paper, oscillate within the crystal against other super-cells of the same kind, forming a repetition pattern of vibrations in which the space-unit is a giant cell having four times the dimensions and sixty-four times the volume of the unit cell of the crystal lattice. *Pro forma* equations of motion may even be framed for the oscillation of such groups and the possible solutions discussed on the same lines for the atomic vibration, giving us eight sets of possibilities of the same kind as those given by (11); one of these, namely that in which all the super-cells vibrate in the same way should be excluded, as this would involve displacements of the centre of inertia of the entire crystal. The 8×3 or 24 degrees of freedom of oscillation of the super-cells contained in the giant cell would thus give us 21 modes of vibration, leaving as before, 3 degrees of freedom to be assigned to still lower frequencies of vibration. In the case of crystals of high symmetry, the number of distinct frequencies thus arising would naturally be reduced much below the maximum of 21.

An approach of the kind suggested above is obviously lacking in rigour, since it leaves the movements of the individual atoms within the oscillating super-cells unspecified. It is however not without value, since it indicates that as we come down the scale of frequency, the vibrations in the lattice may tend to take on the character of group movements which are intermediate in character between the purely atomic vibrations occurring at the high-frequency and the purely mass movements at the low-frequency end.

^{*} Cf. Scientific Papers of the late Lord Rayleigh, Vol. III, Art. 142, Equation (74); *Phil. Mag.*, 1887, 24, 145.

The configuration of the vibrating groups bears a specific relation to the structure of the crystal instead of, as in the elastic vibrations, being determined solely by the form and dimensions of the external boundary of the crystal. It is also clear that the frequencies of the group movements would be related to the size of the groups in much the same way as the frequency of elastic waves is related to their wave-lengths. If such group oscillations exist, as seems not unlikely in the higher ranges of the elastic spectrum, the frequency distribution in the latter would tend to approach the discreteness characteristic of the atomic vibration spectrum, instead of being continuous as indicated by the classical theory of elasticity.

8. *Remarks on Some Earlier Theories*

The close analogy between the vibration-spectra of molecules and of crystals indicated by the foregoing theory receives unmistakeable support from the results of the experimental investigation of crystal spectra by the several distinct methods to which reference has been made earlier in the paper. The results of the present theory are however in striking contrast with the ideas widely prevalent at the present time regarding the nature of the atomic vibrations in crystals. It is necessary, therefore, at this stage to make some critical comments on the earlier views which have found currency in the literature of the subject.

The well-known and closely allied theories of Debye and Born on the atomic vibrations in solids were put forward about the same time (1912) in order to explain their thermal behaviour at low temperatures. As was shown earlier by Einstein in 1907, however, the frequencies of the atomic vibrations which constitute the thermal energy of a solid lie in the infra-red region of the electromagnetic spectrum. It follows that the evaluation of the specific heat of a solid must depend on a knowledge of its spectroscopic properties in the infra-red frequency region. The experimental spectroscopic data for solids available in 1912 were, however, of a very meagre description. This may have been the reason why Debye and Born sought a different path from that indicated by Einstein and endeavoured to calculate the specific heat of solids by identifying their thermal energy with the energy of elastic vibrations of all possible frequencies. However, recent spectroscopic studies with many crystals, including especially several of the simplest chemical composition, show this identification to be unjustifiable. For, *they reveal numerous characteristic or monochromatic frequencies lying in the remotest infra-red*, in other words, within just the region which was sought to be described as a continuous spectrum of elastic vibration frequencies.

Both Debye and Born assumed that the normal modes of atomic vibrations have the same relation to the external dimensions of the solid as do the vibrations of the elastic type. This assumption is not, however, a reasonable one, since the modes and frequencies of the *mass* movements involved in elastic vibration and the modes and frequencies of *atomic* vibration depend on wholly different factors. These are the macroscopic properties and dimensions of the solid for the former, while for the latter they are the individual masses of the atoms and the manner in which they are arranged and bound together in the fine structure of the crystal. The considerations already set out above indicate that the external boundary of the solid can have no determining influence either on the normal modes or the normal frequencies of the atomic vibrations. On the other hand, the size and shape of the solid is the principal factor in determining the normal modes and frequencies of its elastic vibrations.

It is thus evident that theoretical considerations and experimental facts alike compel us to reject the assumptions on which the Debye and the Born theories are based.

9. Born's Postulate of the Cyclic Lattice

In the Born theory, the lattice structure of the crystal is formally taken into consideration on the basis of the so-called "Postulate of the Cyclic Lattice".* This postulate assumes the *phase* of the vibration to alter progressively along each of the axes of the Bravais lattice in such manner that the "phase-wave-length" is a sub-multiple of an arbitrary chosen length which is itself a large integral multiple of the lattice spacing. Thus, for each axis, the number of possible phase-wave-lengths is equal to the number of lattice spacings contained in the given length, and when all the three axes are considered, the total number of possibilities becomes equal to the total number N of lattice cells contained in the assumed large volume of the crystal. When multiplied by $3p$ (the number of degrees of freedom of motion of the atoms in each cell), the total number of possibilities is increased to $3Np$. Each of these is assumed to represent a possible normal mode of vibration with a corresponding frequency. Since the lengths of the "phase-waves" are assumed to be the various sub-multiples of an arbitrarily assumed large multiple of the lattice spacing, they bear no simple relation to the crystal spacings themselves. Indeed, the phase-wave-lengths postulated crowd up increasingly as they become smaller, and hence the vast majority of them have values *intermediate* between small integral

* *Problems of Atomic Dynamics*, by Max Born, 1926, p. 193.

multiples of the lattice spacing. It is not surprising therefore that the Born theory yields an immense array of frequencies which form a diffuse continuous spectrum and which correspond to the assumed practically infinite array of possible phase-wave-lengths.

From the statement made above regarding the Born postulate,[†] it will be evident that it is equivalent to taking the ratios α , β , γ considered in Section 4 of the present paper as imaginary quantities, viz.,

$$\alpha = e^{i\phi}, \beta = e^{i\psi}, \gamma = e^{i\chi} \quad (12)$$

As already pointed out however, such an assumption would be illegitimate, since in any normal mode the phase of vibration must everywhere be either the same or the opposite, in other words, the only possible values of ϕ , ψ , χ are either 0 or π , making α , β , γ equal to either plus or minus unity, as indicated in our equation (11). If, on the other hand, it be suggested that equation (12) does not refer to a normal vibration but only to a "wave" in the lattice, then before it could be used for calculating the possible frequencies of atomic vibration, it would be necessary to show that the real amplitudes obtained by superposing on it another "wave" in the opposite sense given by

$$\alpha = e^{-i\phi}, \beta = e^{-i\psi}, \gamma = e^{-i\chi} \quad (13)$$

would satisfy the requirements for a normal vibration. The result of superposing the "waves" represented by (12) and (13) would be to give a vibration of which the amplitude is proportional to the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ where l_1 , l_2 , l_3 are the three cell index-numbers counted respectively along the three axes. As already remarked, however, Born's phase-wave-lengths bear no simple relation to the crystal spacings, and hence the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ and therefore also the energy of vibration would vary from cell to cell within the crystal. This is a state of affairs which cannot possibly exist in a normal vibration, and it follows that except when ϕ , ψ and χ are each chosen equal to 0 or π , the Born phase-waves do not correspond to any real or possible normal modes of vibration. Thus, it is evident that the whole immense arrays of atomic frequencies given by the Born theory are "manufactured" by his assumption of modes of vibration which are physically impossible and that they do not possess any physical meaning or significance.

The Born postulate is in the clearest contradiction with the experimental facts observed in crystals. As an illustration, we may choose the case of diamond in view of the simplicity of its structure. The unit cell of

[†] *Handbuch Der Physik, Zweite Auflage*, Article by Max Born and M. Goppert-Mayer, 1933, 24/2, p. 642.

the diamond lattice contains two atoms, and the Born theory would therefore yield a continuous spectrum with two optical and two acoustic branches, and hence exhibiting (at the most) four diffuse peaks or maxima. On the other hand, according to the present theory, the atomic vibrations in the 8-cell super-lattice would have $(2 \times 24 - 3)$ or 45 modes, but on account of the high symmetry of the crystal, the number of distinct frequencies would be reduced to 8. The highest of these frequencies represents the oscillation of the two interpenetrating lattices in the crystal against each other and appears as a sharp and intense line with a frequency-shift 1332 cm.^{-1} in the spectrum of the scattering of light by diamond. The remaining seven modes of lower frequency are longitudinal or transverse oscillations against each other of the planes of equivalent atoms in the crystal lying parallel to the faces of the cube and the octahedron. Several distinct methods of investigation of the lattice spectrum of diamond are available, the results of which are an independent check on each other. The spectroscopic studies of P. G. N. Nayar* show the existence of a whole series of discrete frequencies from 1332 cm.^{-1} downwards, and the values for these frequencies as deduced from the scattering, fluorescence and absorption spectra are in complete agreement with each other. While Nayar's experimental results find a natural explanation on the theory set forth in the present paper, they are wholly irreconcilable with the Born postulate and its consequences.

10. Summary

Starting from the most general expression for the potential energy of the displacements of the atoms in a crystal from their positions of equilibrium, their normal modes of vibration are derived. It is shown that in all the possible modes, the equivalent atoms in the crystal have all the same amplitude of vibration and either the same phase or alternately opposite phases in the successive cells of the lattice along each of its three edges. The vibrations thus form a repeating pattern in space of which the unit has twice the dimensions and eight times the volume of the lattice cell. The vibration modes are closely analogous to that of a molecule with the appropriate symmetries and containing eight times the number of atoms included in the lattice cell. The spectrum thus consists of a discrete set of monochromatic frequencies, the number of which is finite and is further reduced when the crystal belongs to a highly symmetric class. The small residue of degrees of freedom not included in this description appears as quasi-elastic vibrations having specifiable low frequencies.

* P. G. N. Nayar, *Proc. Ind. Acad. Sci.*, 1942, **15**, 293.

NORMAL OSCILLATIONS OF THE DIAMOND STRUCTURE

BY S. BHAGAVANTAM

(From the Department of Physics, Andhra University, Guntur)

Received October 25, 1943

1. Introduction

IN an earlier paper, Venkatarayudu¹ has used group theoretical methods to show that the primary normal oscillation of the diamond structure consists of a mutual displacement of the two interpenetrating lattices, the direction of displacement being arbitrary. This analysis and similar work in respect of other crystals already published by the author and Venkatarayudu² are based on the fundamental assumption that the smallest unit or the Bravais cell of the structure is the repeating pattern both from the static and from the dynamic points of view. That the next stage in the analysis would be to consider a super-lattice of which the cells have twice the edge length of the smallest cell and that the oscillations thus derived would have also to be reckoned in formulating the basic theory of crystal dynamics and of the thermal energy of crystalline solids was pointed out by Raman.³ In a paper* now under publication, Raman⁴ is giving a proper theoretical foundation for the idea of the super-lattice frequencies put forward by him earlier.

In this paper, group theoretical methods are applied to the case of diamond and the results appropriate to a repeating unit which has eight times the volume of the smallest unit cell are given. This repeating unit is formed by taking twice the primitive translation as the side of the cell along each direction instead of the primitive translation itself. Such a cell contains 16 carbon atoms whereas the smallest one contains only 2.

2. Diamond Structure and its Symmetry Operations

In Fig. 1 is shown a portion of the diamond structure which is made up of two interpenetrating lattices. The dark circles denote atoms belonging to one lattice whereas the white circles denote the atoms belonging to the other. The smallest unit cell is a rhombohedron formed by the primitive translations 1, 2; 1, 3 and 1, 4. Such a rhombohedron contains only two

* An advance copy of this paper has been very kindly sent by Professor Raman to the present author.

distinct atoms which are numbered 1 and 5. In such a case translations 1, 2; 1, 3 and 1, 4 cannot be regarded as distinct from the identity operation

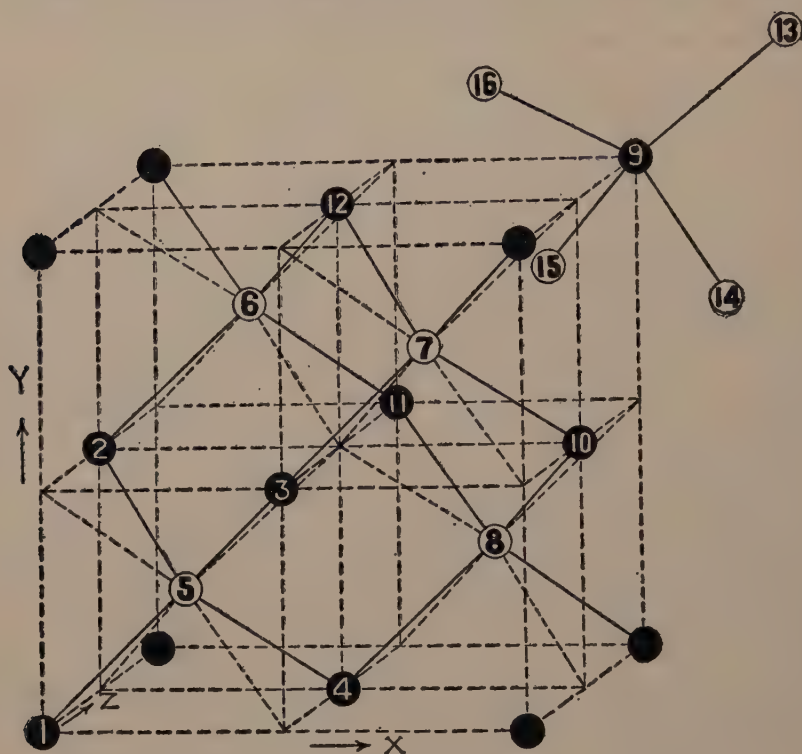


FIG. 1

and all the atoms numbered 2, 3, 4, 9, 10, 11 and 12 are equivalent to 1, whereas those numbered 6, 7, 8, 13, 14, 15 and 16 are equivalent to 5. The symmetry group will then consist of 48 elements only and has been dealt with earlier. The unit cell chosen in this paper is, however, a larger rhombohedron formed by the primitive translations which are twice 1, 2; 1, 3 and 1, 4. Such a rhombohedron contains 16 distinct atoms which are numbered 1 to 16 in Fig. 1. Besides the 48 elements of the simple group, seven translations (1, 2; 1, 3; 1, 4; 1, 9; 1, 10; 1, 11; 1, 12), which were hitherto identical with the identity element, have now to be regarded as distinct symmetry operations. These, along with the identity operation, constitute a sub-group of order 8 and the total group of symmetry operations appropriate to the diamond structure in which there are 16 non-equivalent points as shown in Fig. 1, will be formed by obtaining the product of the simple 48 elements with the above translational group consisting of 8 elements. The resulting group is of order 384. The elements of this group fall into

20 conjugate classes* and the appropriate character table is given here. Notation used is similar to that employed in the earlier papers of the author. The table shows that besides the translation, there are one threefold, three sixfold, two fourfold and two eightfold degenerate normal oscillations coming under various symmetry classes.

If all the last six columns and the last six rows are deleted, we get the character table containing only fourteen conjugate classes and if the number of elements in each conjugate class is properly adjusted, we get results that are appropriate to a group of 192 elements which refers to the case where the smallest cubic cell containing 8 atoms only is regarded as the repeating unit.†

3. Normal Modes and Normal Frequencies

Below is given one representative mode under each class. Those omitted may be written down from considerations of symmetry and taking into account the order of degeneracy in each case and the manner in which each normal co-ordinate transforms under the different symmetry operations. If the normal co-ordinates given below are read with reference to Fig. 1, it is easy to get a physical picture of each one of the modes.

$(x_1 + x_2 + x_3 + x_4 + x_9 + x_{10} + x_{11} + x_{12})$					
$-(x_5 + x_6 + x_7 + x_8 + x_{13} + x_{14} + x_{15} + x_{16})$	F ₂
$(x_1 + x_2) - (x_3 + x_4) + (x_9 + x_{10}) - (x_{11} + x_{12})$	H ₁
$(x_1 - x_2 + x_3 - x_4) + (y_5 - y_6 + y_7 - y_8) + (x_9 - x_{10} + x_{11} - x_{12})$					
$+ (y_{13} - y_{14} + y_{15} - y_{16})$	H ₂
$(x_1 - x_2 + x_3 - x_4) - (y_5 - y_6 + y_7 - y_8) + (x_9 - x_{10} + x_{11} - x_{12})$					
$- (y_{13} - y_{14} + y_{15} - y_{16})$	H ₄
$(p_2 + p_3 + p_4 + p_6 + p_7 + p_8 + p_9 + p_{13})$					
$-(p_1 + p_5 + p_{10} + p_{11} + p_{12} + p_{14} + p_{15} + p_{16})$	K ₁
$(p_2 + p_3 + p_4 - p_6 - p_7 - p_8 + p_9 - p_{13})$					
$-(p_1 - p_5 + p_{10} + p_{11} + p_{12} - p_{14} - p_{15} - p_{16})$	K ₃
$-(x_1 - z_1) + (x_2 - z_2 + x_3 - z_3 + x_4 - z_4) + (x_9 - z_9)$					
$-(x_{10} - z_{10} + x_{11} - z_{11} + x_{12} - z_{12}) - (x_5 - z_5) + (x_6 - z_6$					
$+ x_7 - z_7 + x_8 - z_8) + (x_{13} - z_{13}) - (x_{14} - z_{14} + x_{15} - z_{15}$					
$+ x_{16} - z_{16})$	M ₁
$-(x_1 - z_1) + (x_2 - z_2 + x_3 - z_3 + x_4 - z_4) + (x_9 - z_9) - (x_{10} - z_{10}$					
$+ x_{11} - z_{11} + x_{12} - z_{12}) + (x_5 - z_5) - (x_6 - z_6 + x_7 - z_7 + x_8 - z_8)$					
$- (x_{13} - z_{13}) + (x_{14} - z_{14} + x_{15} - z_{15} + x_{16} - z_{16})$	M ₂

* Writing down all the 384 elements in the form of circular permutations and classifying them into conjugate classes is a very laborious process but follows the well-known methods of group theory. Details are not given here as they would occupy much space.

† This case had been fully worked out last year by the author in collaboration with Dr. T. Venkatarayudu but the results remained unpublished.

In K_1 and K_3 , p stands for a displacement x, y, z . The frequencies of these modes can be evaluated in the usual manner. Below is given a statement which shows the frequency in each case and contains a description of the corresponding normal mode.

	Mode	Degeneracy	$\frac{4\pi^2 \nu^2}{m}$
F_2	One interpenetrating lattice oscillating against the other.	3	$\frac{8K_1}{3m} + \frac{64K_2}{3mp^2}$
H_1	Consecutive planes parallel to the cube faces of any one lattice moving along the cubic axis normal thereto in opposite directions.	6	$\frac{4K_1}{3m} + \frac{40K_2}{3mp^2} + \frac{8K_3}{m}$
H_2	Consecutive planes parallel to the cube faces of any one lattice moving transverse to the cubic axis normal thereto in opposite directions while those of the second lattice do the same thing but in phase.	6	$\frac{12K_2}{mp^2} + \frac{4K_3}{m}$
H_4	“ “ “ “ while those of the second lattice do the same thing but in opposite phase.	6	$\frac{8K_1}{3m} + \frac{4K_2}{3mp^2} + \frac{4K_3}{m}$
K_1	Consecutive planes parallel to the 111 faces of any one lattice moving along the (111) axis normal thereto in opposite directions while those of the second lattice do the same thing but in phase.	4	$\frac{2K_1}{3m} + \frac{64K_2}{3mp^2} + \frac{8K_3}{m}$
K_3	“ “ “ “ while those of the second lattice do the same thing but in opposite phase.	4	$\frac{2K_1}{m} + \frac{8K_3}{m}$
M_1	Same planes as in K_1 now move transverse to the (111) axis and hence acquire twice the degeneracy.	8	$\frac{8K_1}{3m} + \frac{34K_2}{3mp^2} + \frac{2K_3}{m}$
M_2	Same as in M_1 but planes belonging to the two lattices are in opposite phase.	8	$\frac{6K_2}{mp^2} + \frac{2K_3}{m}$

K_1 and K_3 are respectively the force constants referring to any pair of atoms which constitute the nearest neighbours and the next nearest neighbours. K_2 represents the force called into play when the angle between any two valence bonds which meet at an atom varies. p stands for the distance between a pair of nearest neighbours and is the same as the length of the valence bond.

In conclusion, the author desires to express his thanks to Sir C. V. Raman with whom he had the opportunity of discussing this subject on several occasions.

Summary

Group theoretical methods have been applied for obtaining the normal oscillations of the diamond structure on the basis of a 16 atom cell as the repeating unit. It is shown that besides the translation, there are eight normal oscillations one of which is threefold degenerate, two of which are fourfold degenerate, three of which are sixfold degenerate and two of which are eightfold degenerate. Expressions are derived for the corresponding normal frequencies by postulating suitable potential energy functions.

REFERENCES

- | | |
|--|--|
| 1. Venkatarayudu, T. | .. <i>Proc. Ind. Acad. Sci., A</i> , 1938, 8 , 349. |
| 2. Bhagavantam, S., and
Venkatarayudu, T. | <i>Ibid.</i> , 1939, 9 , 224. |
| 3. Raman, C. V. | .. <i>Ibid.</i> , 1941, 14 , 459. |
| 4. ——— | .. <i>Ibid.</i> , 1943, 18 , 237. |

THE NORMAL VIBRATIONS IN SOME TYPICAL CUBIC CRYSTALS

BY E. V. CHELAM

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received October 25, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

BHAGAVANTAM AND VENKATARAYUDU (1939) investigated the modes of atomic vibration in various crystals, employing group-theoretical methods. The starting point of their work was the proposition that the vibration-pattern repeats itself in every cell of the crystal lattice. On this basis, $(3p - 3)$ normal modes are possible, p being the number of non-equivalent atoms in the lattice cell. Crystals consisting of a single Bravais lattice, *e.g.*, various metals, would have no *discrete* frequencies of atomic vibration, while cubic crystals such as rock-salt and diamond containing two non-equivalent atoms in the cell would have only one such frequency representing a triply degenerate mode of vibration. In the introductory paper of this symposium, it has been shown, however, by Sir C. V. Raman that besides the modes considered by Bhagavantam and Venkatarayudu, there are $21p$ others, and that a super-cell having twice the dimensions and eight times the volume of the unit cell of the crystal lattice is the basis of the repeating pattern of all the modes of atomic vibration except those which may properly be classified as elastic vibrations of the lattice. The complete description of these modes and the determination of their activity or inactivity in light-scattering and infra-red absorption should be possible with the aid of group-theoretical methods as applied to the atoms contained in the super-cell. The classification of the possible modes into 8 different sets characterised by different phase-relations between the successive equivalent atoms along the three axes of the Bravais lattice should considerably simplify this task. The use of the phase-relations and of the geometric description of the modes of vibration to which they lead however enables us to indicate the normal modes for crystals of not too complex a structure by quite elementary methods. Of particular importance are the cases in which the crystal possesses the symmetry of the cubic system, and the number of non-equivalent atoms in its lattice is not large, being only one, two or three.

2. Vibrations of Face-Centred Lattices

We shall first consider the case of the face-centred cubic lattice which is of importance in view of the fact that it forms the basis of the structure

of numerous crystals. As is well known, the unit cell of the lattice in this case is a rhombohedron, the six faces of which are parallel to the octahedral planes in the complete cubic crystal. The planes cutting the three axes of the cell at equal angles are also parallel to the faces of the octahedron. The planes which pass through one rhombohedral axis and *internally* bisect the angle between the other two axes are parallel to the dodecahedral faces, while the planes passing through one axis and *externally* bisecting the angle between the other two are parallel to the cube faces. As explained by Sir C. V. Raman in the introductory paper of the symposium, the geometric character of the atomic movements may be described in terms of these planes. The possible modes fall into one or another of the eight sets given by the relations.

$$\alpha = \pm 1, \beta = \pm 1, \gamma = \pm 1,$$

where α, β, γ are the amplitude ratios of the vibrations of successive equivalent atoms respectively along the three axes of the super-lattice cell.

The case in which α, β, γ are all positive, which we may denote by the symbol $(+ + +)$, represents translations of the cell as a whole. It is thus excluded from the scheme of normal vibrations and goes over to the "elastic spectrum" of the crystal. The four cases represented by the symbols $(- + +)$, $(+ - +)$, $(+ + -)$ and $(- - -)$ of which the meaning should be obvious represent movements in which the *alternate* planes of atoms parallel to the *octahedral* faces oscillate against each other. Each case has three degrees of freedom associated with it, and the total of 12 degrees of freedom accordingly falls into 4 groups, each with three degrees of freedom representing different directions of movement. A *longitudinal* oscillation of the planes, *i.e.*, a movement along the trigonal axis which is their normal, clearly stands on a different footing from *transverse* oscillations of the planes. For the latter, all directions lying in the octahedral planes are clearly equivalent, and we may therefore choose any two orthogonal directions.

The cases $(- - +)$, $(+ - -)$ and $(- + -)$, each with 3 degrees freedom, may be described as movements of the planes of atoms parallel to the *cube* faces. It is then easy to see that the 9 degrees of freedom associated with these modes fall into two distinct groups. In one group, the alternate planes of atoms parallel to the cube faces oscillate *longitudinally*, while in the other group they oscillate *transversely*. We have thus *four* distinct frequencies of vibration of the atoms contained in the super-cell; the degeneracies associated with them, together with the three translations of the super-cell total up to 24 degrees of freedom.

		Degeneracy
(1) Translations	3
(2) The octahedral planes vibrate longitudinally	4
(3) The octahedral planes vibrate transversely	8
(4) The cubic planes vibrate longitudinally..	3
(5) The cubic planes vibrate transversely	6
		<hr/>
	TOTAL ..	24

3. The Zincblende Lattice

In this crystal, the zinc and sulphur atoms form face-centred cubic lattices which interpenetrate each other, their relative displacement along the trigonal axis being one-fourth of the length of the body-diagonal. We have 24×2 or 48 degrees of freedom in all. There are four layers of atoms (alternately Zn and S) in the super-cell parallel to the octahedral and cubic planes. From the general considerations set out by Sir C. V. Raman in the introductory paper of the symposium, it follows that the oscillations of the structure are obtained by doubling up the modes derived above for a face-centred lattice, one set representing movements of the adjacent zinc and sulphur atoms in the same phases, while in the other set they are in opposite phases. We may, in fact, immediately write down the modes with *nine* distinct frequencies arising in this way, the degeneracies associated with them together with the three translations of the super-cell totalling to 48 degrees of freedom.

					Degeneracy
(1) Translations	3
(2) Oscillation of the zinc and sulphur lattices against each other					3
(3) Oscillation of the octahedral planes of atoms normally with the phases	+	+	-	-	4
	Zn	S	Zn	S	
(4) Same as (3) but with the phases	+	-	-	+	4
	Zn	S	Zn	S	
(5) Oscillation of the octahedral planes of atoms transversely with the phases	+	+	-	-	8
	Zn	S	Zn	S	
(6) Same as (5) but with the phases	+	-	-	+	8
	Zn	S	Zn	S	
(7) Oscillations of the cubic planes of atoms normally with the phases	+	+	-	-	3
	Zn	S	Zn	S	
(8) Same as (7) but with the phases	+	-	-	+	3
	Zn	S	Zn	S	
(9) Oscillation of the cubic planes tangentially with the phases	+	+	-	-	6
	Zn	S	Zn	S	
(10) Same as (9) but with the phases	+	-	-	+	6
	Zn	S	Zn	S	
					<hr/>
	TOTAL ..				48

4. *The Diamond Lattice*

The case is clearly similar to that of the zincblende lattice except that we have now two similar atoms instead of two dissimilar ones. There are four similar layers of carbon atoms in the super-cell parallel to the octahedral planes and also parallel to the cubic planes. The spacing of the layers parallel to the octahedral planes is alternately greater and smaller, and hence the similarity of the two atoms leaves unaffected the distinctness of the frequencies of the modes in which the layers closer to each other move respectively with the same or opposite phases. On the other hand, the four layers of atoms present in the cubic planes are equidistant, and the question therefore arises whether the movements of these planes fall into two distinct sets or merge into one. An examination of a model of a crystal shows however that in respect of oscillations in a direction *normal* to the cubic planes, all the four successive layers are symmetrically and identically circumstanced. Hence, the modes in diamond analogous to those listed as (7) and (8) for the case of zincblende have identical frequencies. On the other hand, the situation is different for oscillations *transverse* to the cubic planes. *Alternate* pairs of atoms in the planes parallel to the cubic faces appear laterally displaced with respect to each other. Hence, the modes of oscillation in which the closely adjacent layers of carbon atoms move transversely with the same or the opposite phases are quite distinct and their frequencies are different. We have accordingly the following scheme of normal vibrations for diamond, giving *eight* distinct frequencies.

	Degeneracy
(1) Translations	3
(2) Oscillation of the two interpenetrating lattices against each other	3
(3) Oscillation of the octahedral planes of atoms normally with the phases + + - -	4
(4) Same as (3) with the phases + - - +	4
(5) Oscillation of the octahedral planes of atoms transversely with the phases + + - -	8
(6) Same as (5) with the phases + - - +	8
(7) Oscillation of the cubic planes of atoms normally with the phases or + - - +	6
(8) Oscillation of the cubic planes of atoms transversely with the phases + + - -	6
(9) Same as (8) with the phases + - - +	6
TOTAL ..	48

5. The Rock-Salt Lattice

Here, the sodium and chlorine ions form face-centred lattices which interpenetrate in such a manner that in the octahedral planes, the two sets of ions appear separately in alternate and equidistant layers, while in the cubic planes, they also appear in equidistant layers, but interspersed. The five sets of possibilities for the case of a face-centred lattice therefore get doubled up as in the case of zincblende, but the description of the modes would be different owing to the altered nature of the atomic arrangements. It is evident that the layers of sodium ions lying in the octahedral planes can oscillate against each other independently of the chlorine ions, and *vice versa*. On the other hand, in the cubic planes, the oscillations of the two sets of ions are necessarily coupled with each other. We have thus the following scheme for the rock-salt lattice giving *nine* distinct frequencies.

	Degeneracy
(1) Translations	3
(2) Oscillation of the sodium and chlorine lattices against each other	3
(3) Oscillation of the sodium layers against each other normally to the octahedral planes	4
(4) Oscillation of the chlorine layers against each other normally to the octahedral planes	4
(5) Same as (3) but transversely	8
(6) Same as (4) but transversely	8
(7) (a) } Coupled oscillation of the sodium and chlorine ions normally to the	3
(7) (b) } cubic planes	3
(8) (a) } Coupled oscillation of the sodium and chlorine ions tangentially to the	6
(8) (b) } cubic planes	6
TOTAL ..	48

6. The Fluorspar Lattice

The fluorite structure differs from that of zincblende and diamond in having *three* interpenetrating face-centred lattices instead of two, all the eight places within the cubic cell being occupied by the F ions instead of four being empty as in the diamond structure. We have in all 24×3 or 72 degrees of freedom, and the modes of vibration may be derived from those of a face-centred lattice by considering the three possible alternatives; (a) the Ca and the two F ions are all in the same phase of vibration; (b) the Ca ion is one phase and the two F ions in the opposite phase; and (c) the two F

ions move in opposite phases, the Ca ions being at rest. In the octahedral planes, the Ca and F ions appear in distinct layers at unequal intervals, each Ca layer having two F layers disposed symmetrically on either side. On the other hand, in the cubic planes, the atoms appear in equidistant layers, the Ca ion and the F ions jointly occupying the alternate layers. We have accordingly the following scheme of normal modes for the fluorite lattice, giving us fourteen distinct frequencies of vibration.

							Degeneracy
(1) Translations	3
(2) Oscillation of the Ca lattice jointly against the two F lattices	3
(3) Oscillation of the two F lattices against each other, the Ca lattice being at rest	3
(4) Oscillation of the octahedral planes normally against each other with the phases		+	+	+	-	-	-
		F	Ca	F	F	Ca	F
(5) Same as (4) with the phases	..	-	+	-	+	-	+
		F	Ca	F	F	Ca	F
(6) Same as (4) with the phases	..	+		-	-		+
		F		F	F		F
(7) Same as (4) but transversely			8
(8) Same as (5) but transversely			8
(9) Same as (6) but transversely			8
(10) Oscillation of the cubic planes normally with the phases		+	+	-	-		
		Ca	F ₂	Ca	F ₂		
(11) Same as (10) with the phases	..	+	-	-	+		
		Ca	F ₂	Ca	F ₂		
(12) Same as (10) with the phases	..	-	+	+	-		
		F	F	F	F		
(13) Same as (10) but transversely			6
(14) Same as (11) but transversely			6
(15) Same as (12) but transversely			6
TOTAL							72

7. The Vibrations of Body-Centred Lattices

The unit rhombohedral cell in this case has its faces parallel to *three* of the dodecahedral planes of the cubic crystal, while the planes which pass through one rhombohedral axis and internally bisect the angle between the other two are also *three other* dodecahedral planes orthogonal to the first set. It follows that all the six cases (+ + -), (+ - +), (- + +),

(+ - -), (- + -) and (- - +), each of which is associated with 3 degrees of freedom, represent movements of the planes of atoms lying in the dodecahedral planes alternately in opposite phases. There are 6 such planes, and allowing three orthogonal directions of movement in each case, a total of 18 degrees of freedom is accounted for. The three orthogonal directions of movement of the atoms lying in a dodecahedral plane are evidently (1) normal to it and parallel to a face-diagonal; (2) tangential to it and parallel to a cube-edge and (3) tangential to it and parallel to a face-diagonal, and these represent distinct cases. The case (+ + +) represents translations of the super-cell, while the case (- - -) represents an oscillation of all the atoms located at the cube-corners moving in the same phase against all the atoms located at the body-centres moving together in the opposite phase.

The 24 degrees of freedom of the atoms contained in the super-cell have accordingly to be grouped in the following manner, giving *four distinct* frequencies.

	Degeneracy
(1) Translations	3
(2) Oscillations of the alternate dodecahedral planes against each other normally to themselves along a face-diagonal of the cube	6
(3) Oscillations of the alternate dodecahedral planes against each other tangentially to themselves along a cube edge ..	6
(4) Oscillations of the alternate dodecahedral planes against each other tangentially along a face-diagonal of the cube ..	6
(5) Oscillations of the body-centre atoms against the cube-corner atoms in any three orthogonal directions	3
	—
TOTAL .. .	24

8. The Cæsium Chloride Lattice

This structure consists of two simple cubic lattices interpenetrating each other in such manner that the Cs ions are located at the body-centres of the cubic lattice formed by the Cl ions and *vice versa*. As a preliminary to the discussion of this case, therefore, we have to write down the modes of vibration for a simple cubic lattice.

The following scheme of modes for a simple cubic lattice is almost self-explanatory in view of the preceding detailed consideration of the face-centred and body-centred lattices.

	Degeneracy
(1) Translations	3
(2) Cubic planes vibrating alternately in opposite phases, normally	3
(3) Same as (2) but tangentially	6
(4) Dodecahedral planes vibrating alternately in opposite phases tangentially along a cube axis	3
(5) Dodecahedral planes vibrating alternately in opposite phases along the two dodecahedral axes in the perpendicular plane	6
(6) Octahedral planes vibrating alternately in opposite phases in three orthogonal directions	3
TOTAL ..	24

The introduction of a second interpenetrating lattice will result in all these six possibilities being doubled up, corresponding respectively to the cases in which the two adjacent non-equivalent atoms vibrate in the same phase or in opposite phases. It may be remarked that in the cubic planes the Cs and the Cl ions appear alternately in distinct and equidistant layers. Accordingly, we have the following scheme of normal vibrations for the CsCl lattice.

	Degeneracy
(1) Translations	3
(2) The Cs and the Cl lattices vibrate against each other along any 3 orthogonal directions	3
(3) The Cs ions in the cubic planes vibrate against each other with alternate planes in opposite phases, normally ..	3
(4) Same as (3) but tangentially	6
(5) Movement of the chlorine layers in the alternate cubic planes against each other, normally	3
(6) Same as (5) but tangentially	6
(7) } Coupled oscillations of the Cs and Cl ions in the dodecahedral planes with alternate planes	3
(8) } vibrating normally in opposite phases	3
(9) } Same as (7) but tangentially	6
(10) }	6
(11) Alternate Cs layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions	3
(12) Similar motion as above of the chlorine layers	3
TOTAL ..	48

The author wishes to record here his indebtedness to Sir C. V. Raman, Kt., F.R.S., N.L., under whose kind guidance and encouragement the above work was conducted.

Summary

The normal modes of vibration of the simple cubic, body-centred and face-centred lattices as well as of the zincblende, diamond, rock-salt, fluor-spar and caesium chloride lattices have been derived by simple geometric methods on the basis of the fundamental ideas set out by Sir C. V. Raman in the introductory paper of the symposium. It is shown that the lattices mentioned have 5, 4, 4, 9, 8, 9, 14 and 11 distinct frequencies respectively.

REFERENCES

- | | |
|--|--|
| S. Bhagavantam and
T. Venkatarayudu | <i>Proc. Ind. Acad. Sci. A</i> , 1939, 9 , 224. |
| See also S. Bhagavantam | .. <i>Ibid.</i> , 1941, 13 , 547. |
| Sir C. V. Raman | .. <i>Ibid.</i> , 1943, 18 , 237. |
| See also Sir C. V. Raman | .. <i>Ibid.</i> , 1941, 14 , 459. |

MODES OF ATOMIC VIBRATION IN THE FOURTEEN BRAVAIS LATTICES

BY G. N. RAMACHANDRAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 5, 1943

(Communicated by Sir C. V. Raman, K.T., F.R.S., N.L.)

Introduction

IN the first paper in this symposium, Sir C. V. Raman has discussed the normal modes of vibration of a crystal lattice, and has come to the conclusion that, in a normal mode, the atoms in adjacent cells must vibrate either in the same or opposite phases. In other words, starting from any atom, if one proceeds to an equivalent atom in the next cell by any one of the three primitive translations, the latter atom must vibrate with a phase either the same as or opposite to that of the former. If we represent the ratio of the amplitudes of atoms in adjacent cells along the three principal directions by α , β and γ , then these can take only the values $+1$ or -1 . Also, the value of α , β or γ must be the same for *all* the non-equivalent atoms in the unit cell, if the equations of motion are to be satisfied. Hence, in the general study of the vibrations of crystal lattices, we may, as a first step, apply these ideas to determine the nature of the vibrations for the fundamental Bravais lattices.

It is, no doubt, true that few crystals possess the simple Bravais lattices for their structure; but any crystal can be built out of a number of such lattices interpenetrating one another. Then, the values of α , β and γ will be the same for every one of the non-equivalent atoms in the unit cell, and the vibrations will pertain to the same type as those for the simple lattice. Obviously, each mode of the simple lattice will be split up into p modes, if there are p atoms per unit cell. These will have to be determined by making use of the condition that all the p atoms in the cell must vibrate in either the same, or opposite phases, and also that the relative phases of the atoms must be identical in every cell. But a consideration of the relative phases alone is not sufficient in a general case, and one has to take into account the force system, etc. However, in some simple cases with a relatively small number of atoms occupying special positions in the lattice, a consideration of phase relations alone may suffice to enable the modes to be described more or less completely.

It is clear that a complete description of the modes, and the determination of the corresponding frequencies is, in general, not possible unless one has a knowledge of the nature of the interatomic forces in the crystal lattice. But even in the absence of such information, the symmetry of the lattice brings about a reduction in the number of discrete modes. Thus, if the application of a symmetry operation pertaining to the lattice brings one mode into coincidence with another, then the two must have identical frequencies. Since it is only the *direction* of the axes along which α , β and γ have the prescribed values that is important, one can dispense with the translation group of the space-lattice altogether, and consider only the point-group that is located at each of the lattice points. The only symmetry operators that need be considered are those that belong to this point-group, which is a sub-group of the space-group. Hereafter, by the word "operator" will only be meant a symmetry-operator of the point-group.

The description of a normal mode by the conditions $\alpha = \pm 1$, $\beta = \pm 1$, $\gamma = \pm 1$ shows that there are eight possible types of motion in the most general case, with $3p$ degrees of freedom for each, if there are p atoms in the unit cell. Of these $24p$ degrees of freedom, 3 will represent the translation of the lattice as a whole along three directions, and the remainder $(24p - 3)$ will be the number of vibrational degrees of freedom. In the present case, p is equal to unity, and the number of distinct modes of vibration will be 21 in the general case of a lattice with no symmetry. But if the lattice has some special symmetries, then it is found that the eight types are not distinct, and that some of them may be identical. Thus, they can be classified into a lesser number of sets, where the types in any set give identical frequencies.

The directions of vibration of the three modes in each type can be found as follows. Suppose that the atoms are vibrating in a particular mode. Out of the point-group of operations which brings the lattice into self-coincidence, choose one which brings atoms of the same phase into coincidence, *for that mode*. Then, the mode of vibration after applying this symmetry operation must be the same as the one before. Hence, the directions of vibration in the two cases must either be the *same* or *equivalent*. This must be true for the whole group of symmetry-operations which brings atoms of the same phase into self-coincidence. This group of operations, which may be called the group of that type of vibration, either leaves the directions of vibration invariant, or brings them into one another. We may therefore take the following as a working rule for obtaining all the information about the directions of motion that is possible by using only considerations of symmetry:

For each type of motion, involving a particular combination of α , β , γ , determine all the symmetry operations which bring atoms of the same phase into self-coincidence. With a postulated set of directions for the vibration, find if the directions are left invariant, or brought into one another. In the former case, the vibrations are non-degenerate, but if one direction is brought into another, the vibrations in these directions have the same frequency, and if all the directions are interchanged, the vibration is triply degenerate. If, on the other hand, none of the above possibilities occurs, and a direction is brought into none of the three postulated ones, then it cannot be a direction of motion for the normal mode. Another set of directions is then postulated, and the method is repeated. In this way, not only are the directions of motion determined, but the degeneracies for the vibrations in the type are also known.

For the sake of convenient reference, we shall tabulate the directions of motion and their degeneracies when the group of the type of vibration is one of certain point-groups which will be needed in this paper. The point-groups that come in are all those of the holohedry in each system. The results tabulated here could also be checked by making use of rigorous group-theoretical methods. In the second column are shown the states to which the vibrations belong, and the number of modes coupled in each. These have been arrived at by the standard method of using character tables.

Point-group	States of the vibrations	Description of the directions of vibration
C_1 ..	3 coupled in A_u	Three directions unspecifiable.
C_{2h} ..	1 in A_u and 2 coupled in B_g	One direction along the 2-fold axis, and the other two undetermined, lying in the plane perpendicular to it.
D_{2h} or V_h ..	1 in B_{1u} , 1 in B_{2u} , and 1 in B_{3u}	The three directions are orthogonal, and are along the directions of the three 2-fold axes.
D_{4h}	1 in A_{2u} and 1 in E_u	One direction along the 4-fold axis, and the other two degenerate in the perpendicular plane.
D_{3d} ..	1 in A_{2u} and 1 in E_u	One direction along the 3-fold axis, and the other two degenerate in the perpendicular plane.
D_{6h} ..	1 in A_{2u} and 1 in E_{1u}	One direction along the 6-fold axis, and the other two degenerate in the perpendicular plane.
O_h ..	1 in T_{1u}	The vibration is triply degenerate.

Using the above general methods, the modes of vibration will now be worked out for the fourteen Bravais lattices. The primitive translations will

be represented by OA, OB and OC, and α , β , γ will respectively pertain to these three directions.

1. Triclinic Lattice Γ_{tr}

This lattice has the highest symmetry of the triclinic system, *i.e.*, that of triclinic holohedry, C_i . The symmetry operations are identity 1 and inversion I. The latter only reverses the direction of the primitive translations, which however does not alter the value of α , β or γ . Hence, no two modes are identical, and there are 21 distinct modes of vibration falling into 7 types. These types can be described as the vibration of atoms in alternate crystallographic planes with opposite phases. Each has three degrees of freedom, but the direction of vibration for these cannot be specified from considerations of symmetry alone, for the group of every one of the eight types is C_i , which brings any direction into self-coincidence. The description of the modes is given below:

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	-	Vibration of atoms in alternate (001) planes with opposite phases along three unspecified directions ..	1, 1, 1
7 to 9	+	-	+	Same as (4) to (6), but of alternate (010) planes ..	1, 1, 1
10 to 12	-	+	+	Same as (4) to (6), but of alternate (100) planes ..	1, 1, 1
13 to 15	-	-	+	Same as (4) to (6), but of alternate (110) planes ..	1, 1, 1
16 to 18	-	+	-	Same as (4) to (6), but of alternate (101) planes ..	1, 1, 1
19 to 21	+	-	-	Same as (4) to (6), but of alternate (011) planes ..	1, 1, 1
21 to 24	-	-	-	Same as (4) to (6), but of alternate (111) planes ..	1, 1, 1
Total ..					24

Number of discrete modes of vibration **21**.

2. Simple Monoclinic Lattice Γ_m

This has the highest symmetry of the monoclinic system, namely that of the point-group C_{2h} . The symmetry operators are the identity 1, $A(\pi)$, S_h and $A(\pi)S_h$, where $A(\pi)$ denotes a 2-fold axis along the z -axis, and S_h a horizontal reflection plane normal to it, containing the x and y axes. Two of the primitive translations OA and OB are taken in the symmetry plane along Ox and Oy respectively, and the third OC is taken perpendicular to them along Oz. Obviously, the application of every one of the symmetry operations only brings the axes into self-coincidence, or reverses their direction, neither of which alters the value of α , β or γ . Hence, here also, we have 21 distinct modes of vibration, but the directions of some of these can be specified. The group of every one of these is verified to be C_{2h} , so

that one direction is along the 2-fold axis Oz , and the other two lie in the plane xOy .

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4	+	+	-	Vibration of atoms in alternate (001) planes with opposite phases, normally to the planes	1
5, 6	+	+	-	Same as (4), but transversely in two undetermined directions in the plane	1, 1
7 to 9	+	-	+	Vibration of atoms in alternate (010) planes along three directions, one parallel to Oz and the other two in the plane xOy	1, 1, 1
10 to 12	-	+	+	Same as (7) to (9), but of (100) planes	1, 1, 1
13 to 15	-	-	+	Same as (7) to (9), but of (110) planes	1, 1, 1
16 to 18	-	+	-	Same as (7) to (9), but of (101) planes	1, 1, 1
19 to 21	+	-	-	Same as (7) to (9), but of (011) planes	1, 1, 1
22 to 24	-	-	-	Same as (7) to (9), but of (111) planes	1, 1, 1
Total					24

Number of distinct modes of vibration **21**.

3. Side-Centred Monoclinic Lattice Γ_m'

In this lattice two opposite sides have atoms at the centre in addition to Γ_m . The primitive translations, as also the directions of the crystallographic axes are marked out in Fig. 1. This lattice has also the point-group symmetry of C_{2h} , and the application of the symmetry operations results in the following:

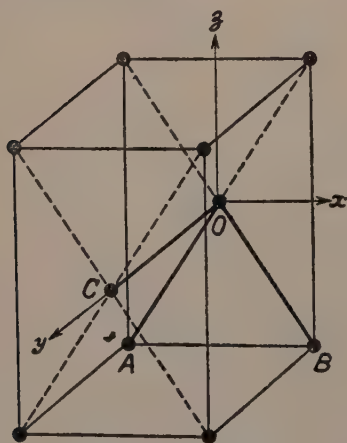


FIG. 1. Side-centred Monoclinic Lattice

1 leaves the primitive translations unaltered, and if we denote the new values of α , β , γ , by α' , β' , γ' , respectively, then $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

S_h converts $OA \rightarrow -OB$, and $OB \rightarrow -OA$, leaving OC unaltered. Hence, $\beta' = \alpha$, $\alpha' = \beta$, $\gamma' = \gamma$.

$A(\pi)$ has the same effect on α , β , γ as S_h , and

$A(\pi) S_h$ produces no changes in α , β , γ .

If we work out the effect of these transformations on the eight combinations of α , β and γ , then it is found that $+-+$ and $-++$ are equivalent, and that so are

+ - - and - + -, the rest being distinct. The group of these four is only C_2 so that the directions of vibration cannot be specified. For the rest, the group of the vibration is C_{2h} , and one direction is along Oz , the other two lying in xOy . The modes of vibration can, therefore, be described as follows:

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	-	Vibration of the atoms in alternate (010) planes in three directions, one along Oz , and the other two in the plane xOy	1, 1, 1
7 to 9	-	-	+	Same as (4) to (6), but of (100) planes	1, 1, 1
10 to 12	+	-	+	} Vibration of atoms in alternate $(10\bar{1})$ and (101) planes with opposite phases in three undetermined directions	2, 2, 2
	-	+	+		
13 to 15	+	-	-	} Same as (10) to (12), but of $(11\bar{1})$ and (111) planes	2, 2, 2
	-	+	-		
16 to 18	-	-	-	Same as (4) to (6), but of (011) planes	1, 1, 1
Total ..					24

Number of distinct modes **15**.

4. *Simple Orthorhombic Lattice Γ_o*

This lattice has the full symmetry of the orthorhombic system, *i.e.*, of the point-group V_h or D_{2h} . The symmetry operations are 1, U, V, W; S_h , US_h , VS_h , WS_h , where U, V, W are respectively rotations through π about 2-fold axes along Ox , Oy , Oz , and S_h is a reflection on the xy plane. The primitive translations may be taken along Ox , Oy and Oz , so that none of the symmetry operations alters the value of α , β or γ . Thus, for this lattice also, there are 21 modes of vibration, but the directions of the vibration can be specified for all of them, since the group of all the eight types of vibration is D_{2h} .

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	-	Vibrations of atoms in alternate (001) planes with opposite phases along the directions Ox , Oy , Oz ..	1, 1, 1
7 to 9	+	-	+	Same as (4) to (6), but of (010) planes	1, 1, 1
10 to 12	-	+	+	Same as (4) to (6), but of (100) planes	1, 1, 1
13 to 15	-	-	+	Same as (4) to (6), but of (110) planes	1, 1, 1
16 to 18	-	+	-	Same as (4) to (6), but of (101) planes	1, 1, 1
19 to 21	+	-	-	Same as (4) to (6), but of (011) planes	1, 1, 1
22 to 24	-	-	-	Same as (4) to (6), but of (111) planes	1, 1, 1
Total ..					24

Number of distinct modes **21**.

5. Side-Centred Orthorhombic Lattice Γ_0'

This lattice has, in addition to the simple orthorhombic lattice, two points at the centres of two opposite sides. The unit cell of the lattice is shown in Fig. 2, where OA, OB, OC are the primitive translations, and Ox, Oy, Oz are the orthorhombic axes.

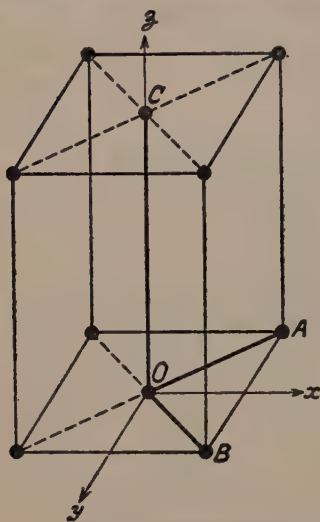


FIG. 2. Side-centred Orthorhombic Lattice

This lattice also has the pointgroup symmetry of V_h , and the application of the symmetry operations produces the following transformations:

1 leaves α , β , γ unaltered.

U makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

V makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

W leaves α , β , γ unaltered, and S_h also does the same, so that $S_h U$, $S_h V$, $S_h W$ have the same effect as U, V, W respectively.

Hence, out of the eight combinations of α , β and γ , only 6 are distinct, two pairs being equivalent, viz., $(+ - +, - + +)$; $(+ - -, - + -)$. For these four types,

the group is C_{2h} , while for the rest it is V_h . The modes of vibration can, therefore, be described as below :

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	-	Vibration of atoms in alternate (001) planes with opposite phases along the directions Ox , Oy , Oz ..	1, 1, 1
7 to 9	-	-	+	Same as (4) to (6), but of (100) planes	1, 1, 1
10 to 12	-	-	-	Same as (4) to (6), but of (101) planes	1, 1, 1
13 to 15	+	-	+	Vibration of atoms in alternate (110) and ($\bar{1}\bar{1}0$) planes along three directions, one along Oz , and the other two in the plane xOy	2, 2, 2
	-	+	+		
16 to 18	+	-	-	Same as (13) to (15), but of ($\bar{1}\bar{1}1$) and (111) planes..	2, 2, 2
	-	+	-		
Total ..					24

Number of distinct modes of vibration **15**.

6. Body-Centred Orthorhombic Lattice Γ_0'''

This lattice has, in addition to the simple lattice Γ_0 , a point at the centre of its unit cell. The primitive translations can be taken as the line joining the centre O to three of the corners A, B, C as shown in Fig. 3. The ortho-

rhombic axes Ox, Oy, Oz will be parallel to the sides of the rectangular parallelepiped. The translation along the fourth direction OD to the adjacent atom may be represented by $(\vec{OA} + \vec{OB} + \vec{OC})$, and the phase change for the translation will be the product of those for OA, OB and OC , i.e., equal to $\alpha\beta\gamma$. This lattice has also the symmetry of the point-group V_h , and the application of the symmetry operations of this group results in the following:

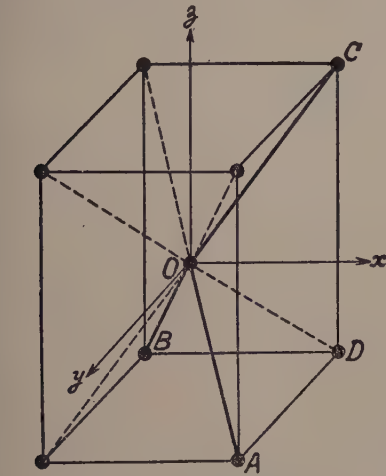


FIG. 3. Body-centred Orthorhombic Lattice

- 1 leaves α, β, γ unaltered.
- U makes $\alpha' = \gamma, \beta' = \alpha\beta\gamma, \gamma' = \alpha$.
- V makes $\alpha' = \alpha\beta\gamma, \beta' = \gamma, \gamma' = \beta$.
- W makes $\alpha' = \beta, \beta' = \alpha, \gamma' = \alpha\beta\gamma$.
- S_h makes $\alpha' = \beta, \beta' = \alpha, \gamma' = \alpha\beta\gamma$.
- $S_h U$ makes $\alpha' = \alpha\beta\gamma, \beta' = \gamma, \gamma' = \beta$.
- $S_h V$ makes $\alpha' = \gamma, \beta' = \alpha\beta\gamma, \gamma' = \alpha$.
- $S_h W$ makes $\alpha' = \alpha, \beta' = \beta, \gamma' = \gamma$.

On working out the effect of these transformations on the eight combinations of α, β and γ , the following sets become identical: $(++-, --+); (+-+, -+-); (+--, -++)$. For these six types, the group of the vibration is only C_{2h} , while for $(+++)$ and $(---)$, it is V_h . Hence, the modes of vibration are the following:

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	-	-	-	Vibration of the two lattices, composed of the atoms at the centre, and of atoms at the corners, against one another with opposite phase, parallel to Ox, Oy and Oz	1, 1, 1
7 to 9	+	+	-	Vibration of atoms in alternate (110) and $(1\bar{1}0)$ planes along three directions, one parallel to Oz , and the other two lying in the plane xOy	2, 2, 2
10 to 12	+	-	+	Same as (7) to (9), but of (011) and $(01\bar{1})$ planes along Ox and two other directions in yOz	2, 2, 2
13 to 15	+	-	-	Same as (7) to (9), but of (101) and $(10\bar{1})$ planes along Oy and two other directions in zOx	2, 2, 2
Total					24

Number of distinct modes 12.

7. Face-Centred Orthorhombic Lattice Γ_0''

This lattice has, in addition to the simple orthorhombic lattice, atoms at the centres of the six faces. The primitive translations \vec{OA} , \vec{OB} , \vec{OC} can be taken as the lines joining a corner to the centres of three faces intersecting at that corner, as shown in Fig. 4. The translations to the centres of the other three sides will be $(\vec{OB} - \vec{OC})$, $(\vec{OC} - \vec{OA})$ and $(\vec{OA} - \vec{OB})$, and the phase changes for these translations are $\beta\gamma$, $\gamma\alpha$ and $\alpha\beta$ respectively. Applying the symmetry operations of the point-group V_h , to which the lattice belongs, to the eight combinations of α , β , γ , we find that

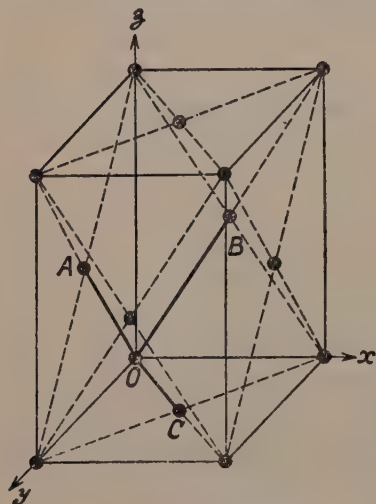


FIG. 4. Face-centred Orthorhombic Lattice

1 leaves α , β , γ unaltered.

U makes $\alpha' = \alpha$, $\beta' = \gamma\alpha$, $\gamma' = \alpha\beta$.

V makes $\alpha' = \beta\gamma$, $\beta' = \beta$, $\gamma' = \alpha\beta$.

W makes $\alpha' = \beta\gamma$, $\beta' = \gamma\alpha$, $\gamma' = \gamma$.

S_h makes $\alpha' = \beta\gamma$, $\beta' = \gamma\alpha$, $\gamma' = \gamma$.

$S_h U$ makes $\alpha' = \beta\gamma$, $\beta' = \beta$, $\gamma' = \alpha\beta$.

$S_h V$ makes $\alpha' = \alpha$, $\beta' = \gamma\alpha$, $\gamma' = \alpha\beta$.

$S_h W$ makes $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

Working out these transformations, the following become equivalent $(++-, +-+, -++, ---)$, and the other four are left invariant. The group of the vibration in this set of four is only C_i , so that the directions cannot be specified. For the rest, the group is V_h , and the vibrations take

place along Ox , Oy , Oz . The modes of vibration can be described as below:

No.	α	β	γ	Description	Number of modes
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	-	-	Vibration of atoms in alternate (100) planes along Ox , Oy , Oz with opposite phases	1, 1, 1
7 to 9	-	+	-	Same as (4) to (6), but of (010) planes	1, 1, 1
10 to 12	-	-	+	Same as (4) to (6), but of (001) planes	1, 1, 1
13 to 15	+	+	-	Vibrations of atoms in alternate (111), $(1\bar{1}1)$, $(11\bar{1})$, $(\bar{1}11)$ planes in three unresolvable directions	4, 4, 4
	+	-	+		
	-	+	+		
	-	-	-		

Total number of distinct modes 12.

Total .. 24

8. Simple Tetragonal Lattice Γ_t

This lattice possesses the full symmetry of the tetragonal system, *i.e.*, of the point-group D_{4h} . The symmetry-operations are 1, $A(\pi/2)$, $A(\pi)$, $A(3\pi/2)$; U , $A(\pi/2)U$, $A(\pi)U$, $A(3\pi/2)U$; S_h , $A(\pi/2)S_h$, $A(\pi)S_h$, $A(3\pi/2)S_h$; US_h , $A(\pi/2)US_h$, $A(\pi)US_h$, $A(3\pi/2)US_h$. Here, A is a four-fold axis along Oz , and U represents a rotation through π about a twofold axis along Ox . S_h denotes a reflection in the plane xOy . We take the primitive translations along Ox , Oy , Oz respectively. Then, the application of U , $A(\pi)$ and S_h does not alter the values of α , β , γ ; but the operations $A(\pi/2)$ and $A(3\pi/2)$ bring about an interchange of α and β , $\alpha \rightleftharpoons \beta$, leaving γ unaltered. Hence, out of the eight combinations of α , β , γ , two become equivalent with two others, *viz.*, $(+ - +, - + +)$; $(+ - -, - + -)$, and there are only six distinct sets. For the four types, $+ - +, - + +, + - -$ and $- + -$, the group of the vibration is V_h , and the directions of vibration are distinct and lie along Ox , Oy , Oz . For the other four, the group is D_{4h} , so that one vibration is along Oz , and the other two are degenerate in the plane xOy . The modes of vibration may therefore be described as follows:

No.	$\alpha \beta \gamma$	Description	Number of modes
1, 2	$+++$	Translation of the lattice as a whole	1, 2
3	$++-$	Vibration of alternate basal (001) planes normally along Oz , with opposite phases	1
4	$++-$	Same as (3), but transversely along Ox and Oy , which are, however, degenerate	2
5	$+ - +$	Vibration of alternate prismatic (100) and (010) planes normally	2
6	$+ - +$	Same as (5), but transversely parallel to the tetragonal axis Oz	2
7	$+ - +$	Same as (5), but transversely along the third perpendicular direction, <i>i.e.</i> , Oy and Ox respectively	2
8	$+ - -$	Vibration of atoms in alternate (101), (011) planes along Oz , with opposite phase	2
9, 10	$+ - -$	Same as (8), but along Ox and Oy	2, 2
11	$- + -$	Vibration of atoms in alternate (110) planes along the 4-fold axis Oz	1
12	$- - +$	Same as (11), but in two directions in the plane xOy , which are degenerate	2
13	$- - -$	Same as (11), but of (111) planes along Oz	1
14	$- - -$	Same as (11), but of (111) planes along two directions in xOy , which are degenerate	2
Total ..			24

Number of distinct modes of vibration 12.

9. Body-Centred Tetragonal Lattice Γ'_t

This lattice has, in addition to the simple lattice Γ_t , an atom at the centre of the square prism, and has the symmetry of the point-group D_{4h} . The primitive translations can be taken, as in the body-centred orthorhombic lattice, to lie along the lines joining the centre to three of the corners. In fact, Fig. 3 will suffice for this lattice, but it must be remembered that Oz is a four-fold axis in this case, and that Ox and Oy are equivalent. The effect of the symmetry operations on the primitive translations is as follows:

1 leaves α, β, γ unaltered.

$A(\pi/2)$ makes	$\alpha' = \gamma,$	$\beta' = \alpha\beta\gamma,$	$\gamma' = \beta.$
$A(\pi)$ makes	$\alpha' = \beta,$	$\beta' = \alpha,$	$\gamma' = \alpha\beta\gamma.$
$A(3\pi/2)$ makes	$\alpha' = \alpha\beta\gamma,$	$\beta' = \gamma,$	$\gamma' = \alpha.$
U makes	$\alpha' = \gamma,$	$\beta' = \alpha\beta\gamma,$	$\gamma' = \alpha.$
$A(\pi/2)U$ makes	$\alpha' = \alpha,$	$\beta' = \beta,$	$\gamma' = \alpha\beta\gamma.$
$A(\pi)U$ makes	$\alpha' = \alpha\beta\gamma,$	$\beta' = \gamma,$	$\gamma' = \beta.$
$A(3\pi/2)U$ makes	$\alpha' = \beta,$	$\beta' = \alpha,$	$\gamma' = \gamma.$
S_h makes	$\alpha' = \beta,$	$\beta' = \alpha,$	$\gamma' = \alpha\beta\gamma.$
$A(\pi/2)S_h$ makes	$\alpha' = \alpha\beta\gamma,$	$\beta' = \gamma,$	$\gamma' = \alpha.$
$A(\pi)S_h$ makes	$\alpha' = \alpha,$	$\beta' = \beta,$	$\gamma' = \gamma.$
$A(3\pi/2)S_h$ makes	$\alpha' = \gamma,$	$\beta' = \alpha\beta\gamma,$	$\gamma' = \beta.$
US_h makes	$\alpha' = \alpha\beta\gamma,$	$\beta' = \gamma,$	$\gamma' = \beta.$
$A(\pi/2)US_h$ makes	$\alpha' = \beta,$	$\beta' = \alpha,$	$\gamma' = \gamma.$
$A(\pi)US_h$ makes	$\alpha' = \gamma,$	$\beta' = \alpha\beta\gamma,$	$\gamma' = \alpha.$
$A(3\pi/2)US_h$ makes	$\alpha' = \alpha,$	$\beta' = \beta,$	$\gamma' = \alpha\beta\gamma.$

Using these, one finds that there are only four distinct sets, the following being equivalent $(++-, --+); (+--, -++), (+-+, -+-)$. Of these, only $(+++)$ and $(---)$ have D_{4h} as the group of their vibration. The group of $(++-)$ and $(--+)$ is V_h , and of the rest, C_{2h} . Hence, the modes of vibration are as follows:

No.	$\alpha \beta \gamma$	Description	Number of modes
1, 2	+++	Translation of the lattice as a whole	1, 2
3	++-	Vibration of atoms in alternate (110), $(1\bar{1}0)$ planes	
	--+	normally, with opposite phase	2
4	++-	Same as (3), but transversely along the tetragonal	
	--+	axis, Oz	2
5	++-	Same as (3), but transversely perpendicular to Oz ..	2
	--+		

No.	α	β	γ	Description	Number of modes
6 to 8	+	-	-	Vibration of atoms in alternate (011), (01 $\bar{1}$) planes along Ox, and two other directions in yOz, and of	
	-	+	+	(101), (10 $\bar{1}$) planes along Oy and two other directions in zOx	4, 4, 4
9	-	-	-	Oscillation of the two lattices composed of the atoms at the centre, and those at the corners, against one another, along Oz	1
10	-	-	-	Same as (9), but along two directions in xOy, which are degenerate	2
Total ..					24

Number of distinct modes of vibration 8.

10. Rhombohedral Bravais Lattice Γ_{rh}

This lattice has the full symmetry of the rhombohedral division of the hexagonal system, *i.e.*, of the point-group D_{3d} . The unit cell and the primitive translations are shown in Fig. 5, where Ox, Oy, Oz are the hexagonal crystallographic axes. The symmetry operations of the point-group D_{3d} are

$$\begin{array}{ll}
 1, A(2\pi/3), A(4\pi/3); & U, A(2\pi/3)U, A(4\pi/3)U; \\
 I, A(2\pi/3)I, A(4\pi/3)I; & UI, A(2\pi/3)UI, A(4\pi/3)UI.
 \end{array}$$

Here, A is a threefold rotation axis along Oz, U is a twofold axis along Ox, and I is the operation of inversion. Of these,

$$A(2\pi/3) \text{ makes } \alpha' = \beta, \beta' = \gamma, \gamma' = \alpha.$$

$$A(4\pi/3) \text{ makes } \alpha' = \gamma, \beta' = \alpha, \gamma' = \beta.$$

$$U \text{ makes } \alpha' = \alpha, \beta' = \gamma, \gamma' = \beta.$$

$$A(2\pi/3)U \text{ makes } \alpha' = \gamma, \beta' = \beta, \gamma' = \alpha.$$

$$A(4\pi/3)U \text{ makes } \alpha' = \beta, \beta' = \alpha, \gamma' = \gamma.$$

I leaves α, β, γ unaltered, so that the other operations produce only similar transformations.

Applying these to the eight combinations of α, β, γ , one finds that they split up into four sets, $(+++); (- - -); (++-, + - +, - + +); (- - +, - + -, + - -)$. The group of the first two sets is D_{3d} , but for the types of vibration in the other two, the group is only C_{2h} , so that the vibration is specifiable in only one direction, the other two lying in a perpendicular plane. The

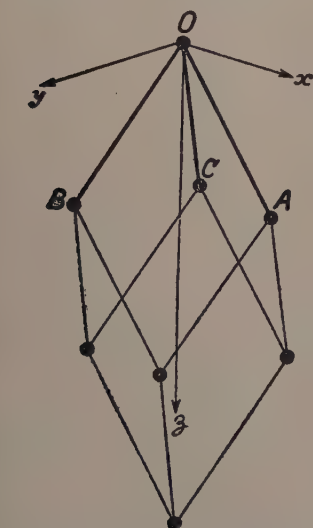


FIG. 5. Unit cell of the Rhombohedral Lattice

modes of vibration may therefore be described as follows, using rhombohedral indices.

No.	α	β	γ	Description	Number of modes
1, 2	+	+	+	Translation of the lattice as a whole	1, 2
3	-	-	-	Vibration of alternate (111) planes normally along the 3-fold axis, Oz	1
4	-	-	-	Same as (3), but transversely, the vibration being degenerate in the plane.. ..	2
5	-	-	+	Vibration of atoms in alternate (1 $\bar{1}$ 0), (10 $\bar{1}$), (01 $\bar{1}$) planes along the normal to the plane	3
6, 7	-	+	-	Same as (5), but transversely in two directions in the plane	3, 3
8 to 10	+	+	-	Same as (5) to (7), but of atoms in alternate (001), (010), (100) planes, which form the sides of the rhombohedral unit cell	3, 3, 3
Total ..					24

Number of distinct modes 8.

11. Hexagonal Bravais Lattice Γ_h

This lattice, which is shown in Fig. 6, has the full symmetry of the hexagonal system, *i.e.*, of the point-group D_{6h} . The symmetry operations are $\{C_6\} \equiv 1, A(\pi/3), A(2\pi/3), A(\pi), A(4\pi/3), A(5\pi/3)$, where C_6 is a sixfold axis parallel to Oz, $\{C_6U\}$, where U is a twofold axis along Ox, $\{C_6S_h\}$ and $\{C_6US_h\}$, where S_h denotes reflection in the plane xOy. The primitive translations

OA, OB, OC lie in this case along the hexagonal axes Ox, Oy, Oz respectively. The effect of symmetry operations on α, β, γ is easily seen to be as below:

1 leaves α, β, γ unaltered.

$A(\pi/3), A(4\pi/3)$ make $\alpha' = \alpha\beta, \beta' = \alpha, \gamma' = \gamma$.

$A(2\pi/3), A(5\pi/3)$ make $\alpha' = \beta, \beta' = \alpha\beta, \gamma' = \gamma$.

$A(\pi)$ makes $\alpha' = \alpha, \beta' = \beta, \gamma' = \gamma$.

U makes $\alpha' = \alpha, \beta' = \alpha\beta, \gamma' = \gamma$.

$A(\pi/3)U, A(4\pi/3)U$ make $\alpha' = \beta, \beta' = \alpha, \gamma' = \gamma$.

$A(2\pi/3)U, A(5\pi/3)U$ make $\alpha' = \alpha\beta, \beta' = \beta, \gamma' = \gamma$.

S_h leaves α, β, γ unaltered, so that the others need not be considered.

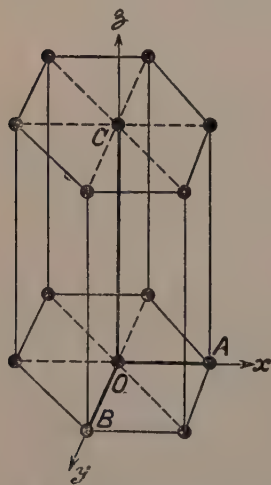


FIG. 6. Hexagonal Bravais Lattice

The combinations of α, β, γ thus reduce to the four sets $(+++)$; $(++-)$; $(+-+)$; $(-+-)$; $(--+)$; $(+-+)$; $(-+-)$.

For the first two types, the group of the vibration is D_{6h} , and for the others it is only V_h . The modes of vibration are, therefore,

No.	α	β	γ	Description	Number of modes
1, 2	+	+	+	Translation of the lattice as a whole	1, 2
3	+	+	-	Vibration of alternate (0001) basal planes against one another normally, along Oz	1
4	+	+	-	Same as (3), but transversely, degenerate in the plane ..	2
5	-	-	+	Vibration of atoms in alternate prismatic planes (01 $\bar{1}$ 0),	
	+	-	+	(1010), (1100) with opposite phases, normally to	
	-	+	+	the plane	3
6	-	-	+	Same as (5), but transversely along the hexagonal	
	+	-	+	axis Oz	3
	-	+	-		
7	-	-	+	Same as (5), but transversely perpendicular to Oz ..	3
	+	-	+		
	-	+	+		
8 to 10	-	-	-	Same as (5) to (7), but of the planes (01 $\bar{1}$ 1), (10 $\bar{1}$ 1),	
	+	-	-	(1 $\bar{1}$ 01) planes along the same directions as in (5)	
	-	+	-	to (7)	3, 3, 3
Total ..					24

Total number of distinct modes 8.

12. Simple Cubic Lattice Γ_c

This, and the next two lattices have been discussed by E. V. Chelam in another paper appearing in this symposium. However, for the sake of completeness, and for a clearer understanding of the methods proposed in this paper, they are also tabulated. The full symmetry operations, and the detailed working will not be given here.

The simple cubic lattice has the highest symmetry of the cubic system, *i.e.*, of the point-group O_h . Taking the primitive translations along the cube axes, an application of the symmetry operations shows that the eight combinations of α , β , γ fall into four sets, $(+++)$; $(---)$; $(++-, +-, +, -+)$; $(- - +, - + -, + - -)$. Of these, the group of the vibrations of the type $(+++)$ and $(---)$ is O_h , so that they are triply degenerate. The group of the remaining six is D_{4h} . The modes of vibration may therefore be described as follows:

No.	α	β	γ	Description	Number of modes
1	+	+	+	Translation of the lattice as a whole	3
2	-	-	-	Vibrations of alternate octahedral (111) planes with opposite phase, triply degenerate	3
3	+	+	-	Vibration of alternate cube faces with opposite phase, normally	3
	+	-	+	
	-	+	+	
4	+	+	-	Same as (3), but transversely, the vibration being degenerate in the plane	6
	+	-	+	
	-	+	+	
5	-	-	+	Vibration of atoms in alternate dodecahedral {110} planes with opposite phase along the cube axis in the plane	3
	-	+	-	
	+	-	-	
6	-	-	+	Same as (5), but along the normal to the plane, and along the third orthogonal direction, <i>i.e.</i> , the dodecahedral axis in the plane, the two being of the same frequency	6
	-	+	-	
	+	-	-	
Total ..					24

Number of distinct modes 5.

13. Face-Centred Cubic Lattice Γ'_c

This lattice has points at the centres of the six cube faces in addition to those at the corners. The primitive translations may be taken as the lines joining a corner to the points at the centre of any three faces intersecting at that corner. Applying the symmetry operations of the point-group O_h to which this lattice belongs, the eight possible combinations of α , β , γ fall into three sets, $(+++)$; $(++-, +-, -, -++)$; $(--+, -+-, +--)$. The group for the vibration in the first set is O_h , that for the second set is D_{3d} and for the third D_{4h} . The vibration in the first set is therefore triply degenerate, and in the other two, one vibration is along the threefold or fourfold axis, and two vibrations are degenerate in the perpendicular plane. The modes of vibration are as follow:

No.	α	β	γ	Description	Number of modes
1	+	+	+	Translation of the lattice as a whole	3
2	+	-	+	Vibration of alternate {111} octahedral planes with opposite phases, normally	4
	+	-	+	
	-	+	-	
	-	-	-	

No.	$\alpha \beta \gamma$	Description	Number of modes
3	$++-$ $+-+$ $-++$ $---$	Same as (2), but transversely degenerate in the plane..	8
4	$---$ $-+-$ $+--$	Vibrations of alternate {100} cube faces normally ..	3
5	$---$ $-+-$ $+--$	Same as (6), but transversely the vibration being degenerate in the plane	6
Total ..			24

Number of distinct modes 4.

14. Body-Centred Cubic Lattice Γ_c''

This lattice has a point at the centre of the cube in addition to Γ_c , and possesses the symmetry of O_h . The primitive translations may be taken along the lines joining the centre to any three of the cube corners. An application of the symmetry operations shows that there are only three sets of combinations of α, β, γ , viz., $(+++)$; $(---)$; $(++-, +-+, -++ , ---, -+-, +--)$. Except the first two, whose group is O_h , the group of all the other six types of vibration is only V_h , so that the vibrations along the three directions are of different frequencies.

No.	$\alpha \beta \gamma$	Description	Number of modes
1	$+++$	Translation of the lattice as a whole	3
2	$---$	Triply degenerate vibration of the two interpenetrating cubic lattices against one another	3
3 to 5	$++-$ $+-+$ $-++$ $---$ $-+-$ $+--$	Vibrations of alternate {110} dodecahedral planes, with opposite phases, in three directions, normally, transversely parallel to a cube axis, and transversely along the dodecahedral axis in the plane ..	6, 6, 6
Total ..			24

Number of distinct modes 4.

The work reported in this paper was undertaken at the suggestion of Prof. Sir C. V. Raman to whom I am extremely grateful for the many helpful discussions I had with him.

Summary

In this paper, the degeneracies and the directions of the normal modes of vibration in the fourteen Bravais lattices are worked out from symmetry considerations, making use of Sir C. V. Raman's theory. Denoting the ratio of the displacements of adjacent atoms along the primitive translations by α , β , γ , these can have only the values $+1$ or -1 , so that the vibrations fall into eight types in the general case of no symmetry. In lattices possessing symmetry, however, some of the types could be brought over into others by the application of symmetry operations, and thus would be equivalent with the latter. Also, the directions of motion in any particular type of vibration may be equivalent. This is determined by selecting a group of operations which brings the atoms of the same phase to coincide for that type of vibration, and finding the directions of motion which satisfy the symmetry requirements of this group. In this way, both the directions of motion and their degeneracies are known. The number of distinct modes of vibration computed for the various lattices, are for Γ_{tr} 21; Γ_m 21, Γ_m' 15; Γ_0 21, Γ_0' 15, Γ_0'' and Γ_0''' 12; Γ_t 12, Γ_t' 8; Γ_{rh} 8, Γ_h 8; Γ_c 5, Γ_c' 4, Γ_c'' 4. The modes are also described in as complete a manner as could be done by using considerations of symmetry alone.

NORMAL VIBRATIONS OF CRYSTAL LATTICES: APPLICATION OF GROUP THEORY

BY E. V. CHELAM

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received November 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

THE usual theoretical investigations of the vibration spectra of dynamical systems (when slightly displaced from an equilibrium configuration) start with some postulated quadratic forms for the kinetic and potential energies. The problem then reduces to a transformation of the quadratic forms to sums of squares, or what amounts to the same thing, to a solution of a set of linear homogeneous equations representing the equations of motion of the system. The sets of solutions so obtained define normal vibrations which represent independent dynamical modes in each of which the system can persist for an indefinite time. In any normal vibration all the constituent atoms of the system necessarily move with the same frequency and with the same or opposite phases.

In a crystal we have to deal with an immense number of similar kinds of atoms all arranged, when in their equilibrium positions, upon a regular triply periodic structure known as the space-lattice. An actual crystal, though finite in extension is very large compared to the inter-atomic distances. When dealing with high frequency interatomic and intercellular vibrations, which obviously depend very largely upon the internal geometric arrangement of the crystal, we are clearly justified in ignoring the boundary and replacing the actual crystal by one with an infinite extension in space. This merely expresses the plausible physical assumption, that, in a crystal with an immense periodic array of atoms, all the corresponding atoms in different unit cells of the lattice stand exactly on the same footing in relationship to their neighbourhood. From a mathematical point of view, this equivalence of the lattice cells in an infinite crystal is expressed by what is usually called 'translational symmetry'. We have to investigate the nature of the normal modes of such a dynamical system.

Now a normal mode of a system represents a state of motion which can continue indefinitely (in the absence of perturbing forces) and independently of other possible modes. It corresponds to a single degree of

freedom of the system and it is therefore sufficient, when describing *any particular normal mode*, to specify the motion of any single atom in that mode. The displacements of all the other atoms *in the particular mode* are not independent quantities, but are uniquely expressible in terms of the displacement of that atom. A normal mode thus carries with it a description of the movement of any particular atom of the system, and the relative displacements of all the other atoms with respect to the particular atom chosen. In the most general case (lack of any symmetry) these relative displacements cannot be computed unless the nature of the forces in the system is known. The expressions for the displacements can only be derived from the equations of motion and involve the various *force constants*. The presence of symmetry in the system however permits us to write down some of these relative displacements at least in some of the normal modes. These relations are a consequence of symmetry only and hold good in any type of force field whatever, provided it leads to a quadratic form for the potential energy. A crystal represents a dynamical system with a high degree of symmetry, namely, the translational symmetry. The lattice as a whole may be displaced vectorially through three primitive lengths (or products or powers of these lengths), and still it returns to self-coincidence. Or, as has been stated earlier, all equivalent* atoms in the lattice stand on exactly the same footing in relationship to their neighbourhood. This equivalence has very important consequences and greatly reduces the complexity of the equations of motion and of the general quadratic form. In the fundamental paper which forms the introduction to this symposium, Sir C. V. Raman has formulated the equations of motion in terms of the most general force constants and has shown that this equivalence at once leads to the theorem that all equivalent atoms must have the same *amplitude* in every truly stationary normal mode. Further, the relative phases can either be the same or opposite with no other possibility. Starting with a particular atom (which for convenience we may locate at a lattice point) we can arrive at the nearest atom equivalent to it along a particular axis by moving through a primitive translation along that axis. According to Sir C. V. Raman, these two atoms have the same amplitude, but the same or opposite phases, in every normal mode. Once the relative displacement of these atoms is thus fixed, the translational symmetry at once fixes the displacement of every other atom equivalent to this along that axis. If the two nearest equivalent atoms have the same phase, the next one should also

* Two atoms are said to be equivalent when they can be brought over into one another by a translation operator, which should also bring the entire crystal into self-coincidence. With this definition the smallest unit cell contains no two equivalent atoms.

have the same phase, and so on. We would thus have a motion of which the phases may be pictured thus:

$$+ + + + + + \quad (1)$$

On the other hand if they have opposite phases, the motion must be like

$$+ - + - + - + - \quad (2)$$

These two results are a consequence of the fact that a primitive translation, being a symmetry element of the lattice does not alter the physical nature of a normal mode. The two possibilities given above arise for translations along one of the primitive axes. The other two axes have two such cases associated with each and the total number of distinct possibilities is thus $2^3 = 8$. In Sir C. V. Raman's notation, these cases are represented by

$$\alpha = \pm 1; \beta = \pm 1; \gamma = \pm 1 \quad (3)$$

Here α, β, γ are the ratios between the displacement of any atom and its nearest equivalent atoms for primitive translations parallel to the axes. If $u_0 (= x_0, y_0, z_0)$ is the displacement any such atom chosen as the basis and u_1, u_2, u_3 , those of the three atoms equivalent to it as above, we have,

$$u_0 = \pm u_1 = \pm u_2 = \pm u_3 \quad [u = x, y, \text{ or } z]. \quad (4)$$

The effective number of independent dynamical variables in the system is thus reduced to the number of degrees of freedom of the set of non-equivalent atoms in the crystal. This is $3p$ if p is the number of non-equivalent atoms in the crystal, and considering the 8 alternative possibilities which go with this set, we may speak of $24p$ dynamical variables which obey the relations (4). The next step is to write down the equations of motion and get the determinantal equation of order $24p$. Either a group theoretical analysis (to be given below), or a simple consideration of the symmetry shows that the eight possibilities are independent, mutually non-combining, and exclusive. Hence these relations can be substituted in the equations of motion one after another, and we get eight different determinantal equations of reduced orders $3p$ each. In the absence of further symmetry, no further reduction is possible and we get $(24p - 3)$ distinct frequencies (excluding 3 for pure translations). All these are different and symmetry is only helpful in separating them into the eight non-combining groups mentioned above. The $3p$ frequencies in each of these groups are coupled, *i.e.*, not separable by symmetry alone. The exact force field must be known to write down the normal co-ordinates and the frequencies for each separately. The presence of further symmetry in the crystal (rotations, reflexions, etc.) simplifies the matters much further and to cover these cases, group theoretical analysis is most helpful, from the point of view of rigour as well as simplicity. These questions will now be discussed.

2. The Symmetry Group

As emphasized earlier, every truly infinite lattice has translational symmetry represented by the three primitive translations, as well as their various products and powers. All these taken together form an Abelian group. In the dynamical problem at hand involving $24p$ dynamical variables only, the translation group assumes a very special character. It will be noticed from relations (1) and (2) that a basis atom has the same amplitude and the same phase as an equivalent atom derivable from it by translations $2\tau_x$, $2\tau_y$, $2\tau_z$ or products and powers of these lengths. The dynamic pattern is thus exactly repetitive in the lattice with a second-order super-cell as the repeating unit. In the investigation of these normal modes, therefore, $2\tau_x$, $2\tau_y$ and $2\tau_z$ are equivalent to identity. If $u_r = (x_r, y_r, z_r)$ is an atom in this super-cell, a translation $2\tau_x$, (or, $2\tau_y$, or $2\tau_z$) carries it into another atom $u_s (= x_s, y_s, z_s)$ which however is identical with u_r in displacement

$$u_r = u_s \quad (5)$$

Hence the effect of the translation $r \rightarrow s$ upon the dynamical variables* is the same as identity and all such translations, their powers and products, can be treated as identity. The translation group thus reduces to the Abelian group defined by

$$\tau_x^2 = \tau_y^2 = \tau_z^2 = E; \tau_x \tau_y = \tau_y \tau_x, \text{ etc.} \quad (6)$$

It has eight operations in all, namely, E , τ_x , τ_y , τ_z , $\tau_x \tau_y$, $\tau_y \tau_z$, $\tau_z \tau_x$ and $\tau_x \tau_y \tau_z$. It will be noted $\tau_x^{-1} = \tau_x$, etc. Any quadratic form for the potential energy which we may formulate must satisfy the symmetry of this group and it follows that the normal modes must come under one or the other of the irreducible representations of this translation group (excluding the case of higher symmetry for a moment). The group being Abelian and of order 8, we must have eight irreducible representations. These are derived easily from the generating relations (6).

$$x(\tau_x) = \pm 1, \quad x(\tau_y) = \pm 1, \quad x(\tau_z) = \pm 1 \quad (7)$$

leading to eight representations.† It is at once evident that (7) expresses the same thing as (3) or (4). Since we know that the normal modes coming under the different irreducible representations of a group are mutually

* It must be remembered that the symmetry operations have significance for us only with respect to their effect upon the dynamical variables.

† See the work of Bhagavantam and Venkatarayudu in this connection (*Proc. Ind. Acad. Sci.*, 1941, 13, 543 : 1939, 9, 224). They have outlined fully the essential technique of group-theoretical analysis for crystals although their investigation is confined to the special case of equality of phase and amplitude for all equivalent atoms, i.e., $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$.

independent and non-combining, it follows that the 8 alternative relations in (4) are independent and can be investigated each by itself. By substituting those relations in the equations of motion, we get, as explained earlier, 8 determinantal equations of order $3p$ each, giving the frequencies. That the $24p$ dynamical variables thus fall into 8 sets with $3p$ in each and that no further reduction is possible is easily verified by applying the standard methods of character tables and reduced characters. Taking the dynamical variables, we notice that each of these is sent into some other variable by the operations of the translation group except the identity which returns every variable to itself. Hence the reduced character of these operations on the dynamical variables is

$$\psi(E)=24p, \quad \psi(T)=0. \tag{8}$$

T stands for any one of the seven translation operations.

Hence the number of normal modes coming under any one of the representations of the translation group is given by

	E	τ_x	τ_y	τ_z	$\tau_x\tau_y$	$\tau_y\tau_z$	$\tau_z\tau_x$	$\tau_x\tau_y\tau_z$	n_i
A ..	1	1	1	1	1	1	1	1	3
B ..	1	-1	1	1	-1	1	-1	-1	„
C ..	1	1	-1	1	-1	-1	1	-1	„
D ..	1	1	1	-1	1	-1	-1	-1	„
B' ..	1	+1	-1	-1	-1	1	-1	+1	„
C' ..	1	-1	1	-1	-1	-1	1	1	„
D' ..	1	-1	-1	1	1	-1	-1	1	„
A' ..	1	-1	-1	-1	1	1	1	-1	„
$\psi_j(R)$	24	0	0	0	0	0	0	0	

the formula $n_i = \frac{1}{N} \sum x_i^j(R) \psi_j(R)$ with the usual notation. It is evident from the table that the $3p$ frequencies in each group cannot be further separated from symmetry considerations alone. With suitably chosen force constants, all the normal modes can be separated and the frequencies calculated.

3. Rotational and Reflexional Symmetry

When a crystal lattice has extra symmetry by way of rotations and reflexions, several interesting features present themselves. In the first place, all the eight sets need not give rise to distinct frequencies. The $3p$ frequencies

in one set can become identical with the frequencies in one or more other sets and we may thus speak of "equivalent" sets. It is sufficient to calculate the frequencies for one such set among a group of equivalent sets, and the labour is thus greatly reduced. The normal co-ordinates corresponding to each other in two equivalent sets can always be brought over into one another by the application of a symmetry operation from the rotational and reflexional symmetry. Hence all the normal modes in the various equivalent sets can also be written from a knowledge of the nature of the modes in one set and the appropriate symmetry operations. A second type of simplification can arise from the fact that if a set of $3p$ frequencies has some other sets equivalent to it, there always exist the possibility of further reduction of the original set from symmetry considerations alone. The determinantal equation of order $3p$ can be further broken up into smaller determinants, using only considerations of symmetry. If the $3p$ modes give rise to s frequencies with varying weightages l, m, n , etc., we get at a very great simplification. Taking a frequency of this set which has a degeneracy of l , we need consider only one of the modes out of the l possible modes. The rest of the l modes give the same frequency and may be omitted from further consideration. Further, it has been explained above that every frequency from this set occurs in all the other sets equivalent to it. If we have r such equivalent sets, this particular frequency has a total number $l \cdot r$ normal modes associated with it, and a consideration of only one mode out of this number is enough to give the frequency. We begin the solution of the dynamical problem, therefore, by taking any one of eight cases given above, and writing down the number of equivalent sets it has. (The method for this is explained in the next paragraph.) If there is a total number r of such equivalent sets, we take only one out of it. Such a set has $3p$ normal modes associated with it, and every frequency from this set is repeated in the $(r-1)$ other equivalent sets and therefore has a minimum degeneracy of r . A further multiplication of degeneracy can arise if the frequency under consideration is the same for more than one out of the $3p$ modes. This type of degeneracy can be determined, and a complete analysis of the $3p$ modes can be made if the symmetry characters appropriate to the particular set under consideration are known. Once an analysis has been made for one such set, it is unnecessary to consider the other equivalent sets, (except to note the total degeneracy) and we may next proceed to consider another set out of the eight which does not occur in the first group of equivalent sets already studied. The number of sets equivalent to it are next noted and the process repeated as above until all the eight cases are fully covered.

The terms "equivalent sets" and "symmetry group appropriate to a set" can be more fully explained now. It will be noticed that each of the eight equivalent sets is defined by the corresponding characteristic values of the three primitive translations, *i.e.*, $\alpha = x(\tau_x)$; $\beta = x(\tau_y)$; $\gamma = x(\tau_z)$. Each case can be specified by giving the values of a vector whose components may be regarded as $x(\tau_x)$, $x(\tau_y)$ and $x(\tau_z)$. The eight vectors are thus given by $(1, 1, 1)$; $(-1, -1, -1)$; $(1, -1, -1)$; $(-1, 1, -1)$; $-1, -1, 1$ and $(1, 1, -1)$; $(1, -1, 1)$; $(-1, 1, 1)$. These correspond, as explained earlier, to the eight irreducible representations of the translation group. In the absence of further symmetry, the frequencies in each set are distinct. Let us now introduce some further symmetry, such as for example a plane of reflexion through the Z-axis bisecting the angle between X and Y axes. This operation keeps the Z-co-ordinate unchanged but changes X to Y and *vice versa*. Since every normal mode represents a state of vibration, it is capable of geometric picturization. If we have two normal modes of vibration, one involving movements of all the atoms along the X-axis and the second a similar movement along the Y-axis, these two modes have the same frequency for a system which has the plane of reflexion mentioned above. The vibration patterns can be carried over into one another by an operation from the symmetry group. This is the essence of degeneracy and in such a case we speak of equivalent modes. Since the eight vectors given above completely specify the nature of the modes for a group of $3p$ frequencies each, it is sufficient to apply the symmetry operations directly to them. The vectors can be given a geometric representation and the set of all vectors carried over into one another by the symmetry operations form an "equivalent set". Under the operation σ_v , $z \rightarrow z$, $x \rightleftharpoons y$, the vectors $(1, 1, 1)$; $(-1, -1, -1)$; $(-1, -1, 1)$; and $(1, 1, -1)$ are unchanged or "left invariant" while $(1, -1, -1)$ and $(-1, 1, -1)$ are carried over into one another with similar effect on the remaining two vectors $(1, -1, 1)$ and $(-1, 1, 1)$. Hence in a system with symmetry σ_v , the eight vectors fall into six distinct sets, and there is a minimum degeneracy of two for every frequency of the last two sets. If the system has got similar reflexion about the X and Y axes also, we get the following system of non-equivalent sets.

- (i) $(1, 1, 1)$
- (ii) $(-1, -1, -1)$
- (iii) $(1, -1, -1)$, $(-1, 1, -1)$; $(-1, -1, 1)$
- (iv) $(-1, 1, 1)$; $(1, -1, 1)$; $(1, 1, -1)$ (10)

We thus need consider only $(1, 1, 1)$; $(-1, -1, -1)$ and one vector each form (iii) and (iv) thus making four in all. Frequencies associated with any

one vector from (iii) are repeated in the other two vectors and so we have a minimum degeneracy of three. If the normal modes associated with $(1, -1, -1)$ say are known, those in $(-1, 1, -1)$ and $(-1, -1, 1)$ are derivable from these by simple application of the reflexion operators through Z and Y axes. A similar statement holds for the modes in (iv).

The easiest method of determining equivalent sets is to directly picture the translation vectors τ_x, τ_y, τ_z instead of their characteristic values. These vectors can be thought of as lying along the three axes and the effect of the symmetry operations upon these is at once evident. Thus σ_y along the Z axis has the following effect on τ_x, τ_y, τ_z .

$$\tau_z \rightarrow \tau_z, \tau_x \rightleftharpoons \tau_y.$$

Hence $x(\tau_z) \rightarrow x(\tau_z); x(\tau_x) \rightleftharpoons x(\tau_y)$.

Applying this operation on the eight representations given in (9), we get straightaway at the distribution given above. The representations A, A', D, D' are left invariant, while B and C are carried over into one another with corresponding results for B' and C'. B and C and similarly B' and C' become "equivalent", under the operation σ_y . We may thus speak of "equivalent" representations instead of equivalent vectors and this language is more suitable to the group theoretical presentation to be given below. If the system has three planes of reflexion about the X, Y and Z axes, the representations B', C' and D' become equivalent and similarly B, C, D also. It must be understood that these representations are not equivalent in the translation group, but become so in the extended group which includes the reflexions. In fact, if the character table for this extended group is written down, it will be noticed that B, C, D combine there in giving rise to a single representation of degree 3. This is a standard method of deriving the character tables and may be employed if we choose to derive the degeneracies and the normal modes straight from the character table for the full group. Actually this introduces unnecessary complications, since all that has been explained before really has the aim of *analyzing* a normal vibration of degree 3 into its constituent vibrations each of degree 1. The process of *compounding* them back again has no importance except to satisfy ourselves that they do really form an equivalent set of representations. Further, the work of Seitz (next section), shows that the modes associated with B can be considered quite independently of the other two equivalent representations C and D. Equivalence brings in the simplification that C and D need not be considered again, while it preserves the original independence of the three representations B, C, D. An investigation of the modes associated with A, A', B and B' is thus quite sufficient to evaluate the frequencies. We will now show how this can be done.

Here we have to explain the significance of the terms "invariance of a vector" (or representation) and the "group of a vector" used in the previous paragraphs. In the example of a group of three planes of symmetry given above, it will be noticed that some of the vectors or representations are changed into themselves by some or all of the symmetry operations. Thus the representations $x(\tau_x) = x(\tau_y) = x(\tau_z) = \pm 1$ are changed into themselves by the three reflexions, while from the very definition, the translations leave every representation of their group invariant. The totality of symmetry operations which leave a vector unchanged is known as *the group of the vector* under consideration. In this case it is the total symmetry group G composed of all the translations and the reflexions. The representation $x(\tau_x) = 1$, $x(\tau_y) = x(\tau_z) = -1$ is however left invariant only by the reflexion plane through the X-axis while the other two reflexions carry it over into the other two equivalent representations. Hence the group of the vector in this case consists of the translations, the reflexion plane σ_x and the other operations derivable by the association of the translations with σ_x . There exist two other similar groups for the other two vectors, derivable by fixing σ_y and σ_z , with the translation group. The structure of the *group* of a vector is of fundamental importance when analyzing the nature of the $3p$ normal modes associated with that vector. It has been shown by Seitz that all representations associated with a vector must come under one or the other of the irreducible representations of the group of that vector. This means that all the $3p$ normal modes going with one vector out of the eight must have the symmetry requirements of one or the other of the irreducible representations of the *group of that vector*. Hence if the structure of this group is known, the normal modes going with this vector are determined by the usual and standard methods. Let the group of this vector be G_1 consisting of operations P, Q, R, etc. We take the $24p$ dynamical variables of the unit cell and study the effect of each of the operations P, Q, R, etc., on these variables. The reduced character $\psi(R)$ of each operation R of this group is thus calculated. From the character table for G_1 , the number of modes coming under any irreducible representation of G_1 is given by the standard formula

$$n_i = \frac{1}{N_1} \sum \psi(R) \chi^i(R). \quad (11)$$

Here N_1 is the order of G_1 and the summation runs over all elements of G_1 .

It will be noticed that G_1 is actually a space group containing translations and as such its character table is not among the standard and well-known tables. A derivation of the table might be attempted, but it is quite

unnecessary for our present work. An alternative elegant method is given in the next section and by its use, the formula is also simplified very greatly. To proceed further however, we need to explain the exact mathematical analysis conducted by Seitz,¹ Clifford,² etc., upon which all the statements made above rest for their validity.

4. Group Theoretical Analysis*

An illuminating treatment of the full mathematical technique needed for the reduction of space groups has been given by Seitz¹ and we note down here only the results of his investigation. For the other points the reader is referred to his original paper. It will be remembered that normal vibrations actually belong to the irreducible representations of the symmetry group of a system. Here we have a space-group composed of rotations, reflexions and translations. So the object is to reduce this group into its irreducible representations, Seitz has actually shown that these representations can be gradually built up starting from the irreducible representations of a translation group. (The translation group is an invariant subgroup of the space-group.) In our present problem these are only eight in number as given in Table 9. The effect of rotational and reflexional symmetry elements upon these representations is such that a particular representation is either completely left invariant (in the sense fully explained already) or totally carried over into another representation which, for this reason, is equivalent to it. This follows, as shown by Seitz, from the Abelian and invariative nature of the translation subgroup. Hence if $\Sigma_1, \Sigma_2, \dots, \Sigma_r$ are such a set of equivalent representations, the effect of the symmetry group on these is to ensure that $\Sigma_r \rightarrow \Sigma_r$ or $\Sigma_r \rightarrow \Sigma_s$ with no linear combination being possible between Σ_r and Σ_s .† From this it follows that the representations of the translation group can be regarded as mutually independent and consideration can be confined to any single representation out of an equivalent set, quite independently of others. The next step is to determine the symmetry characteristics associated with each such representation of the translation group. These are determined by the *group* which leaves the *vector invariant* and its irreducible representations. Seitz has shown that every representation associated with a vector must come under one or the other of the irreducible representations of the group of that vector. As observed earlier, this group is a space-group and sometimes may include the totality of all

* The reader more interested in practical applications of the theory may omit this section and proceed straightaway to the next one where a summary of the whole method is given.

† The emphasis is that we can choose at least one frame of reference in which the representations are of the type indicated above.

the symmetry operations in the crystal lattice, e.g., the (1, 1, 1) vector. The essential point is to build up the representations of a larger group from those of a self-conjugate sub-group in an ascending order, starting from identity and in such a manner that we pass through a series of subgroups of the group of the vector. These subgroups should form a composition series, and in such a series the representations of any group G_r can be derived from the immediate next group G_{r-1} . Every representation G_{r-1} is taken and the effect of the elements of G_r upon it is studied. G_r is actually derivable from G_{r-1} by appending a cyclic group to it. The factor group $\frac{G_r}{G_{r-1}}$ is cyclic and consists of elements, say, E, S, S^2, \dots, S_{n-1} . A particular representation Σ say of degree m of G_{r-1} is chosen and the effect of S upon it is studied. If this representation is left invariant by S, it is left invariant by all the others S^2, S^3, S_{n-1} and the result will be (n) distinct representations in G_r , each of degree m . All these representations have the same characteristics so far as the elements of G_{r-1} are concerned, but differ from one another in the characteristic values of S, S^2 , etc. On the other hand, if S carries Σ into Σ' , the others also do so and we get a set of representations $\Sigma, \Sigma', \Sigma''$ of G_{r-1} which become equivalent in the extended group. All these join together to form an irreducible representation of higher degree in G_r .

So far as our work is concerned, the above mathematical detail is unnecessary except in special cases like the diamond lattice. The only essential point is to notice that these representations are built up starting from the representations of a self-conjugate subgroup which is the translation group in our case. When we are considering the group of a vector, it is enough if we build up only such representations of the translations group as belong to this particular vector. For example, it was observed already that the group of the vector (1, 1, 1) (i.e.) $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$, is the entire space group since it is left invariant by every operation. However, in considering modes associated with this vector, we are not interested in every possible representation of this space group. In the process of building up, we confine our attention only to the representation (1, 1, 1) of the translation group. Only such representations of the space group which are derivable from $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$ by the process of building up as explained above, need be considered. In other words, we have to deal with, firstly, a representation vector of the translation group and secondly, all representation of the group of that vector which are derivable from the original representation of the translation group. These two representations correspond with one another in the two groups and Clifford² calls this correspondence as the representations induced in an invariant subgroup. He

has proved a very elegant theorem showing that all representations in G_1 associated with a definite representation Σ of a self-conjugate subgroup T can be uniquely decomposed as the direct product of two representations, one being Σ itself and the other being an irreducible representation of the factor group G_1/T . The condition is that G_1 should be capable of being written as the product of two groups, one the translation group itself and the other a *point group* of elements. The symmetry of the diamond lattice does not satisfy this condition and exceptional cases like these will be dealt with in a separate paper. In general, this condition is satisfied and Clifford's results show that the representations of G_1 which are associated with a particular representation of the translation group are merely the direct product of that particular representation and an m -fold representation of the point group elements in G_1 . The character tables for all standard crystallographic point groups are known and thus the problem is easily solved. The complexity of the problem is greatly reduced if we choose as dynamical variables the $3p$ displacements only of the atoms in the smallest unit cell. The other $21p$ displacements of the atoms in the neighbouring cells are to be regarded as dependent upon these and expressible in terms of these variable by relations of the type (4). These relations differ from vector to vector, and covering all the 8 cases, we get the total number of degrees of freedom. Considering $3p$ variables only in the unit cell and a specified vector, the reduced character ψ upon these variables can be calculated. Thus if the vector is x (τ_x) = x (τ_y) = x (τ_z) = 1, the effect of each of the translations upon the $3p$ variables in the unit cell (when the state of vibration belongs to the above vector) is to send each variable into another which is the same with respect to it in amplitude and phase. Hence all the variables in the unit cell may be regarded as unchanged by the translation operators in this particular vector.

$$\psi(R) = 3p = \psi(E)$$

for every R of the translation group. The effect of the other operations can likewise be studied. If the vector is x (τ_x) = $-x$ (τ_y) = $-x$ (τ_z) = 1, τ_x keeps the set of $3p$ variables unchanged while τ_y and τ_z change each of them to its opposite phase.

Thus

$$\begin{aligned}\psi(\tau_x) &= 3p = \psi(E) \\ \psi(\tau_y) &= -3p = \psi(E) x(\tau_y) \\ \psi(\tau_z) &= -3p = \psi(E) x(\tau_z)\end{aligned}\tag{12}$$

similarly

$$\psi(\tau_x \tau_y) = +3p, \text{ etc.}$$

From these examples, and simple considerations, it is clear that $\psi(T_n) = \psi(E) x(T_n)$, T_n being an element of the translation group and $x(T_n)$ its

character associated with the vector under consideration. Further, it is obvious that

$$\psi(RT_n) = \psi(R) x(T_n) \quad (13)$$

The results of Clifford show that

$$\begin{aligned} x^i(T_n) &= x^i(E) x(T_n) \\ x^i(RT_n) &= x^i(R) x(T_n) \end{aligned} \quad (14)$$

where R is any element of the point-group symmetry. $x^i(T_n)$ is the characteristic of T_n in the i th representation of the group G_1 which is the group of a specific vector. $x(T_n)$ is the character of T_n for that vector.

Relations (13) and (14) very greatly simplify the formula (11). We have

$$n_i = \frac{1}{N_1} \sum \psi(R) x^i(R) \quad (15)$$

the summation running over all the group elements, *i.e.*, the rotations and reflexions as well as their products with the translations. The summation over the latter can however be entirely dispensed with, by the use of relations (13) and (14). We have,

$$\psi(RT_n) x^i(RT_n) = \psi(R) x(T_n) x^i(R) x(T_n) = \psi(R) x^i(R) \quad (16)$$

since $x(T_n) x(T_n) = 1$ always.

This shows that the product $\psi(R) x^i(R)$ is the same for a parent rotational or reflexional element R as well as its derived operations RT_n for all T_n . Hence the summation over the latter is merely to multiply each term by the number of translation operators. Since the order of the translation group divides the order of the group G_1 the result being the order of the point group element in G_1 , we can express the result as

$$n_i = \frac{1}{m} \sum \psi(R) x^i(R) \quad (17)$$

Here the summation runs over the point group elements of G_1 only and m is their total number. Since Clifford² has shown that the representations of G_1 are the direct product of representations of the translation group with those of $\frac{G_1}{T}$, it follows that $x^i(R)$ belongs to the representations of the point group only. Hence it is no longer necessary to work out the character table for a space group and the information about the point group contained in the group of a vector is quite sufficient to evaluate the normal modes associated with that vector. We shall now briefly summarize all the important points discussed above.

5. Brief Recapitulation

To evaluate the normal modes of a crystal lattice on the basis of the Raman theory of lattice vibrations,³ choose any one of the irreducible representations of the translation group. Find out the symmetry operations, rotations and reflexions which leave this vector unchanged and write down the character table for this point group.* Choose as dynamical variables the $3p$ independent displacements of the atoms in the smallest cell and write down the character ψ of each operation of this point group when acting on these $3p$ variables (during a state of vibration represented by the vector under consideration). Formula (17) then gives straightaway the number of normal modes coming under any one of the irreducible representations of this point group. Their symmetry characters are known from the character table and so the normal co-ordinates can be written down by the usual methods. If the character table for the point group involves representations of degrees 2 and 3 and if the normal modes are not evident at once, we repeat the above process again for this point group. What we have actually done in this work is to analyse the representations of a space group (which are usually of a high degree) into their constituent representations much more convenient to handle. This analysis arises from a choice of the self-conjugate subgroup of the translations. If the point group associated with a vector has representations of degrees 2 or 3, they can be analyzed exactly as above into smaller representations. Once the normal modes are known the frequencies are calculated by the usual methods.†

The next step is to find out the number of representations of the translation group which are equivalent to the vector under consideration. These give the same set of frequencies and only the degeneracy is increased. They need not be considered separately. If these exist $(r-1)$ vectors equivalent to a vector, every frequency associated with it has a minimum degeneracy of r . A frequency with m -fold degeneracy and associated with a vector for which $(r-1)$ other equivalent vectors exist has a total degeneracy of $m \times r$. Investigation of the rest of the vectors is conducted likewise until all the possibilities are exhausted.

The author is extremely obliged to his Professor, Sir C. V. Raman, Kt., F.R.S., N.L., for kind guidance and suggestions throughout the course of this work. He is also indebted to Dr. N. S. Nagendra Nath, M.Sc., Ph.D., and Prof. S. Bhagavantam, M.Sc., D.Sc. (Hon.), for much valuable discussion on the general nature of the harmonic vibrations in a crystal.

* This method is not directly applicable for all the eight phase vectors of a diamond lattice. A simple modification is required which will be dealt with in a separate paper.

† See Bhagavantam and Venkatarayudu's work mentioned earlier.

Summary

A group theoretical method to deal with the harmonic vibrations of a general crystalline lattice is indicated in this paper. Sir C. V. Raman's theory of lattice vibrations³ is the basis of the work and it is indicated how the normal modes, frequencies, their degeneracies, etc., can be rigorously derived. Applications of this work to specific problems are given in another paper in this symposium.

REFERENCES

- | | |
|-------------|--|
| 1. Seitz | .. <i>Ann. of Math.</i> , 1936, 37 , 17. |
| 2. Clifford | .. <i>Ibid.</i> , 1937, 38 , 533. |
| 3. Raman | .. <i>Proc. Ind. Acad. Sc.</i> , A, 1943, 18 , 237. |

RAMAN SPECTRA OF CRYSTALS AND THEIR INTERPRETATION

BY DR. R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 12, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

ITS universal applicability, the simplicity of the technique, the precision of the results obtained and the ease of their interpretation make the Raman effect a powerful instrument for the study of the structure of matter. The information yielded by Raman spectra has been of great value in the investigation of relatively simple molecules as well as of the more complicated polyatomic ones. Its utility in the investigation of the physico-chemical problems set by the crystalline state of matter is equally great. An appreciation of this fact was no doubt responsible for the late Lord Rutherford having stated in his Presidential Address to the Royal Society in December 1930 that the Raman effect "has proved and will prove an instrument of great power in the study of the theory of solids". If this prophecy has not been fulfilled to the maximum extent, it is because the physics of the solid state has been dominated for many years by theories which had their birth before the discovery of the effect, and which, it is safe to say, would probably not have been put forward or received general acceptance if the experimental information furnished by Raman spectra regarding crystals had been available at the time. The reference here is to the well-known theories of solid behaviour originally put forward about the same time (1912) by Debye and by Max Born and which have a common central core in their structure of thought.

It is a significant fact that, subject to some noteworthy qualifications and exceptions, the modes of atomic vibration appearing in the Raman spectra of crystals are represented by sharp lines irrespective of the nature of the substance or of the nature or frequency of the vibrations. In his Faraday Society address of September 1929, Sir C. V. Raman pointedly drew attention to this feature and suggested that the monochromatism of the atomic vibrations is a characteristic consequence of the regular ordering of the ultimate particles in the crystalline state of matter. More recently (1941), he has returned to this subject and put forward a new theory of the specific heat

of crystals in which the basic notions of the Debye and Born treatments are rejected as untenable. In the introductory paper (Raman, 1943) of the present symposium, this new theory has been given a precise mathematical form, and it is shown that every crystal has $(24p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies. Of this number, $(3p - 3)$ modes may be described as oscillations of the p interpenetrating atomic lattices of which the crystal is composed, while the remaining $21p$ modes are oscillations with respect to each other of various important planes of atoms in the crystal. The number of distinct frequencies is considerably reduced when the crystal has a high degree of symmetry. Both the number of frequencies and the geometry of the modes can be fully worked out from symmetry considerations in the case of simple structures. For instance, diamond has eight fundamental frequencies, rock-salt has nine, fluorspar has fourteen, and so forth.

The Raman dynamics of crystal lattices has now reached a form in which it can be worked out and developed in various directions. It is important, however, to show that the ideas on which it is based are well founded, and that on the other hand, the alternative theories which now hold the field are irreconcilable with the experimental facts. It is here that the evidence of the spectroscope is of the highest importance. In another paper appearing in the present symposium, Mr. Pant (1943) has reviewed the extensive and entirely independent evidence available from the published studies on the luminescence and absorption spectra of crystals at very low temperatures. In the present paper, the Raman effect evidence will be marshalled and discussed in its relation to the theories of crystal dynamics.

The numerous papers which have appeared on the Raman spectra of crystals may be placed broadly in two divisions, namely those in which the emphasis is respectively on the chemical and on the physical aspects of the subject. Many more investigations belong to the former group than to the latter, but they have nevertheless yielded data of great significance to crystal physics. The researches on the Raman effect designed expressly to elucidate the fundamental aspects of crystal physics are not very numerous. As we shall see, however, the results they have furnished are quite sufficient to yield a decisive answer to the theoretical issues now under consideration.

2. The Case of Rock-Salt

The Debye theory assumes from the start that the atomic vibrations are of the same general nature as the elastic vibrations of the solid. The Born theory rests on a fundamentally similar assumption, which appears as the so-called "postulate of the cyclic lattice". It is scarcely necessary to discuss

here the Debye theory in detail, as it has no explanation whatever to offer for the appearance of discrete lines in the Raman spectra of crystals. According to Born, the vibration spectrum of the crystal may be divided into branches which he classifies respectively as the "optical branches" and the "acoustic branches", all these, however, being essentially continuous spectra. The experimental fact that the Raman spectra exhibit sharply defined frequencies stands in obvious contradiction with these assumptions. To escape this fundamental difficulty, an ingenious argument has been put forward which we shall examine in detail later in this paper. Before doing so, we shall proceed to consider the actual experimental facts in the case of the rock-salt lattice, which is a particularly suitable substance in view of the fact that much of the work of Born and his collaborators has centred round this substance and its analogues, the alkali halides.

We owe to Rasetti (1929, 1930) the development of a remarkably useful technique for the study of the Raman effect, the value of which has been demonstrated by the resounding success with which he himself applied it in several cases of fundamental interest. In this field of research generally, and especially in investigating substances such as gases or vapours which scatter light only feebly, or crystals which exhibit only feeble Raman spectra, it is essential to employ a light source which emits the most intense possible and highly monochromatic radiation, and that there should be no unwanted radiations and especially no continuous spectrum accompanying the same. Further, it is highly desirable that the exciting radiation (but not the excited ones) should be removed from the light scattered by the medium before its entry into the spectrograph, as otherwise the photographic plates would be fogged by its general diffusion within the instrument. Rasetti secured all these advantages and in addition the enormously increased scattering power of short wave-length radiations arising from the λ^{-4} law, besides enabling the high resolving power which even small quartz spectrographs possess in the ultra-violet region to be utilized, by employing the 2537 Å.U. monochromatic radiations of mercury vapour under special conditions which ensured that *only* this radiation and *none* other would give an observable Raman effect. The technique consists in using a low-pressure quartz mercury arc in which the mercury vapour is prevented from reaching any considerable density, and from absorbing the 2537 radiation emitted by itself. This is accomplished firstly by very effective water-cooling, and secondly by squeezing the discharge against the walls of the quartz tube by the field of a specially designed electromagnet. A filter of mercury vapour at room temperature is placed in the path of the scattered light emerging from the substance under study to absorb the 2537 radiation. This filter works so effectively that

some of the feeble mercury lines which have intensities negligibly small in comparison with the 2537 radiations and which therefore give no observable Raman effect nevertheless appear stronger than the 2537 line in the recorded spectra. This is in particular noticeable with regard to the neighbouring 2535 A.U. line which appears adjacent to the 2537 line in the recorded spectra. In no case, however, does it give any detectable Raman shifts, indeed not even those excited most intensely by the 2537 excitation.

Rasetti investigated many crystals using his technique and with notable success. His greatest achievement in this field was the successful recording of the Raman spectrum of rock-salt which previous investigators had reported as giving no observable effect. The feebleness of the phenomenon can be judged from the fact that with a large prism of rock-salt 5 centimetres thick, an exposure of 8 hours reinforced by internal reflections within the prism had to be given, while a few minutes under the same conditions sufficed for recording the spectrum of quartz. In his preliminary report in *Nature* (1931), Rasetti remarked on the "very peculiar structure" of the Raman spectrum of rock-salt. A rather poor reproduction of the spectrogram appears with his paper in the *Nuovo Cimento* (1932). There is a better reproduction accompanied by a microphotometer record in the joint paper by Rasetti and Fermi (1931) in the *Zeitschrift für Physik*. But the most satisfactory reproduction is that appearing on page 139 of the German translation of Fermi's book *Moleküle und Krystalle* (1938). In this reproduction, the discrete character of the spectrum is quite evident, and the positions of the intensity maxima can be read off from it directly with a glass scale. The details of the structure as thus seen and measured are confirmed by their complete correspondence with the peaks or kinks seen in the microphotometer record appearing immediately above the reproduced spectrogram. A further striking confirmation is furnished by the fact that the pattern is also visible in the reproduction as an "antistokes" Raman spectrum in the extremely clear region lying on the short wave-length side of the 2537 exciting radiation. The details of this region also appear quite distinctly in the microphotometer record.

One notices that the spectrum consists of nine discrete and clearly resolved Raman lines. Their frequency shifts from the exciting 2537 radiation and their approximate widths are recorded in Table I. This shows both the "Stokes" and "antistokes" Raman shifts as determined from the spectrograms and microphotometer records. From the latter records, rough computations have been made of the relative intensities of both the Stokes and antistokes Raman lines. These results are also included in the table. The observed value of the ratio of the intensities of the Stokes

to the antistokes Raman lines is in reasonable agreement with that to be expected from Placzek's well-known formula, as will be seen from the comparison made in the table.

TABLE I
Raman Spectrum of Rock-Salt

Serial Number	Frequency shifts of the Stokes line in cm.^{-1}	Approximate breadth in cm.^{-1}	Relative intensity taking the intensity of 235 Stokes line as 10	Frequency shift of the anti-stokes line in cm.^{-1}	Approximate breadth in cm.^{-1}
1	134	diffuse	3.3	150?	
2	183	25	5.8	189	
3	235	5	10	239	6
4	256	13	8.9	265	
5	281	15	9.9	278	15
6	294	14	10.3	288	15
7	317	14	10	311	15
8	340	8	8.9	339	10
9	350	8	9.2	349	10

Serial Number	Relative intensity taking the intensity of 235 Stokes line as 10	Observed intensity ratio of the Stokes to antistokes line	Calculated intensity ratio using Placzek's formula	Fundamental frequency in cm.^{-1}
1	2.4	1.4	1.9	67
2	2.9	2.0	2.3	91
3	3.2	3.1	3.0	117
4	2.4	3.7	3.3	128
5	2.7	3.7	3.7	140
6	2.8	3.7	3.9	147
7	2.6	3.9	4.3	158
8	2	4.5	4.8	170
9	2	4.6	5.0	175

As will be seen from the figures in the third column of the table, some of the observed lines are quite sharp while others are only moderately so. The line having a frequency shift of 235 cm.^{-1} exhibits exceptional sharpness and intensity both on the Stokes and antistokes sides, and being situated in a clear region and well separated from the remaining lines is a conspicuous feature in the spectrogram. The agreement of the frequency shifts as measured from the Stokes and the antistokes regions, as also of their approximate widths on the two sides, and the fair agreement of the observed intensity ratio of the Stokes to the antistokes lines with that calculated from Placzek's formula leave no room for doubt that the figures shown in the second column are a correct description of the Raman spectrum of rock-salt.

We shall now proceed to examine the facts stated above in the light of the existing theories. As is well-known, the crystal structure of rock-salt is made up of two interpenetrating face-centred cubic lattices. The unit cell is a rhombohedron with one sodium ion and one chlorine ion contained in it. According to Born's theory, a crystal with p non-equivalent atoms in the unit cell would in general have $(3p - 3)$ "limiting frequencies" in the optical branch, the remaining 3 degrees of freedom going to the acoustic branch of the vibration spectrum. The former number may, however, be reduced by the symmetry properties of the crystal to a smaller figure. In the present case $p = 2$, and the crystal belongs to the highest class of cubic symmetry. The 3 possible "limiting frequencies" of the optical branch are therefore reduced by degeneracy to one. As the result of the manner in which the sodium and chlorine ions are grouped around each other, the oscillation of the two sets of ions with respect to each other which has this frequency, would be active in infra-red absorption and would correspond to the reststrahlen frequency of 52μ observed in rock-salt. For the same reason, this vibration should be inactive in the Raman effect. This explains the inability of some of the earlier workers, notably Schæfer (1929) to record any Raman line with rock-salt, and indeed also in the other alkali halides.

Accepting the view-point of the Born dynamics, Fermi attempted to give a theoretical explanation of the observed Raman spectrum of rock-salt in the joint paper by himself and Rasetti (1931) and succeeded to the extent of showing why the high-frequency limit of the Raman spectrum agrees with twice the known reststrahlen frequency of rock-salt. He frankly, however, admitted his inability to explain the other features observed in the spectrum in the following words (translated from the original German):—"In order to calculate the intensity distribution in the Raman spectrum, special assumptions are necessary regarding the influence of the polarisability of the crystal atoms by the elastic displacements. It appears therefore impossible for the present to explain the fine structure of the observed spectrum."

The appearance of nine discrete frequencies in the Raman spectrum of rock-salt, on the other hand, finds a natural and ready explanation in the new theory of the dynamics of crystal lattices put forward by Sir C. V. Raman in the introductory paper in this symposium. In a paper appearing elsewhere in this symposium, Chelam (1943) has worked out the complete vibration spectrum of rock-salt basing himself on the Raman theory of crystal dynamics. The main results of his paper are summarised below. The number of non-equivalent atoms in the rock-salt lattice is 2. Hence the total number of degrees of freedom will be $2 \times 8 \times 3$ or 48, of which 45 will appear as the atomic frequencies and the remaining 3 go over into the

"elastic spectrum". The 45 frequencies would be reduced by degeneracy to 9 distinct ones as shown below:

	Degeneracy
(1) The sodium and chlorine lattices vibrating against each other	4
(2) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(3) The alternate planes of the chlorine atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(4) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, parallel to themselves	8
(5) The alternate planes of chlorine atoms parallel to the octahedral planes oscillating against each other, parallel to themselves	8
(6) & (7) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces, normal to these faces	3 each.
(8) & (9) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces along these planes	6 each.

Because of the symmetry properties of the rock-salt structure, all these nine modes of vibration would be inactive in Raman effect. But it has been pointed out from theoretical considerations by Placzek (1934) and recently by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal vibration is active in the Raman effect, irrespective of whether the fundamental is permitted or forbidden. The observed nine frequencies in the Raman spectrum of rock-salt are therefore the overtones of the nine fundamental modes of vibration enumerated above. The values of these fundamental frequencies calculated from the observed Raman shifts are given in the last column in Table I.

3. *The Structure and Sharpness of the Raman Lines*

In the Raman dynamics of crystal lattices, the monochromatism of the $(24p - 3)$ modes of vibration possible appears as a natural consequence of the fundamental property of crystal structure that it is a three-dimensional repetition pattern in space of practically infinite extension. Any

circumstance that modifies or alters the periodic structure of the crystal must modify the monochromatism of the vibration frequencies to an extent depending on the particular circumstances of the case. An imperfection or mosaicity of the crystal structure and the disturbing influence of thermal agitation may be mentioned as such circumstances. The extent of their influence on the character of the spectra would depend on the individual case, including especially the nature and strength of the binding forces within the crystal, the geometric character of the particular mode of vibration and the masses of the vibrating atoms, ions or molecules. In agreement with these indications of the theory, we find that though Raman spectra of crystals usually consist of well-defined lines with accurately measurable frequency shifts, their sharpness varies from crystal to crystal and even in the same crystal, it may be different for the different lines. It may be and usually is also a function of temperature. Speaking broadly, it may be said that the lines with small frequency shifts are less sharp than the lines with high frequency shifts, but there are numerous exceptions to this rule. Further, there are many examples which suggest that vibrations controlled by valence forces appear as extremely sharp lines in the Raman spectrum, while vibrations controlled by ionic or molecular attractions, appear as rather broad and diffuse lines.

The explanations which have been offered for the appearance of sharp lines in the Raman spectra of crystals on the basis of the Born lattice dynamics may now be briefly stated and examined. They rest on the idea that only the "limiting frequencies" of the lattice, *viz.*, those having great phase-wavelengths could appear in the observed spectra. As a consequence of the postulate of the cyclic lattice, however, vibrations with smaller phase-wave-lengths are enormously more numerous than those with longer phase-wave-lengths, and they would give frequencies different from the latter, and thereby build up a continuous spectrum. What is actually observed in light-scattering, however, is something very different, and to remove this obvious contradiction between the theory and the experimental facts, it is suggested that the frequencies of the vibrations of shorter phase-wave-lengths disappear from the spectrum by reason of the optical interference of the effects due to them arising from different elementary volumes in the crystal. While this argument is no doubt ingenious, it is obvious that it assumes that the atomic vibrations in the lattice have perfectly ordered phase-relations over volume elements sufficiently large for such interference to give, on the one hand the frequencies actually observed with the sharpness and intensities found in experiment, and on the other hand to extinguish completely the frequencies assumed to exist but to be unobservable.

Perhaps the most appropriate comment which could be made is that while, as we have seen in the case of rock-salt, the Born theory does not on the one hand, explain the features actually observed in the spectra, it postulates on the other hand a whole spectrum of frequencies for which there is no observational evidence. Further, to remove the conflict between fact and theory, a hypothetical assumption is made for which there is no experimental justification. In fact, it may be said that the entire approach made in the theory is artificial in character. It should be added that neither *a priori* considerations or any actual facts of observation compel us to assume the existence of coherent phase-relationships of the lattice vibrations of high frequency over extended volumes of the crystal. The mosaicity of most actual crystals, the existence of thermal agitation and above all, the known facts about the thermal conductivity of solids indeed make it difficult to accept such an assumption without large reservations.

4. *The Force-Fields in Crystals*

In not a few cases, the experimental facts established by Raman effect studies with molecular systems, *e.g.*, gases and vapours at ordinary and at higher pressures, liquids, solutions, mixtures and fused melts, form a useful starting point for the interpretation of the phenomena observed with crystals. The greater density and consequently increased magnitude of the force-fields, as also the regular ordering of the units characteristic of the crystalline state have, of course, to be taken into account in this connection. It is obvious also that the classification of molecular movements into three classes as translations, rotations and vibrations, which is quite appropriate for gases and which is not quite so appropriate for liquids ceases to have a strict scientific significance in a crystal. All movements should be considered as atomic displacements and described as time-periodic variations from the standard atomic configurations prescribed by the crystal structure. Indeed no other way of describing the movements is open to us in the case of those crystals in which no specific molecular or ionic configurations can be recognized. With typically molecular or ionic lattices, however, it is convenient to speak of "internal vibrations", "rotational oscillations" and "translatory oscillations", and these descriptions may even roughly correspond to specifiable ranges of vibration frequency. In using these terms, however, it should be remembered that they cannot be an accurate description of the actual displacements in the crystal.

Subject to the limitations indicated, we may consider "ionic" and "molecular" crystals and discuss in turn each of the three classes of vibration. Raman effect studies with liquids, mixtures, solutions and melts show

that the internal vibrations are only influenced in a secondary degree by the state of aggregation. When the irregular arrangements existing in fluids is replaced by the regular ordering characteristic of a crystal, the force-fields surrounding individual ions or molecules become definite. *In consequence, we should expect the "internal frequencies" of the ions or molecules in crystals to become as precisely specifiable as in gases, but with definite changes due to the influence of the force-fields. Indeed, it should be possible to evaluate the changes in these frequencies as between the gaseous, fluid and crystalline states by considering the magnitudes of the force-fields, and vice-versa from the observed frequency changes to evaluate the force-fields.* This principle has been applied with success at this Institute and its utility thereby established.

Raman effect studies in fluid media show that the freedom of rotation of the ions or molecules is greatly hindered in fluids by the density of the aggregation and by the viscosity of the medium. In crystals the molecules or ions occupy specific orientations and the force-fields in which they lie should therefore be exactly definable. Hence the ions or molecules in crystals should have precisely definable frequencies of rotational oscillation about their positions of equilibrium. *From the frequencies of rotational oscillation of optically anisotropic groups as observed in the Raman effect, it should be possible to determine the nature and strength of the force-fields in which they are located. Vice-versa if the force-fields are known, the frequencies of such rotational oscillation could be computed.* This idea again has been applied with success to a number of cases.

Since as stated above, the force-fields in which molecules or ions are located in a crystal are definite, *their translatory oscillations about their positions of equilibrium should also have exactly specifiable frequencies, determined by the masses of the particles and the strength of the fields in which they lie.* In view of the indefiniteness of the force-fields in liquids, we could hardly expect such "translatory oscillations" of the molecules or ions to be observable in the majority of fluid media. Nevertheless, in a few cases, e.g., water and formic acid, they have been observed in the Raman effect as diffuse bands with small frequency shifts. The idea that such translatory movements in crystals should have well-defined frequencies is thereby strengthened. Indeed, there is observational evidence which shows that this is actually the case.

Finally, we may refer to the vibrations of lowest frequency which are essentially mass-movements and are naturally to be regarded as pertaining to the elastic spectrum of the crystal. There would be an immense number of such modes possible in a crystal which would be the more closely crowded together, the lower we go down in the scale of frequency.

Summary

An examination of the spectrograms of the Raman effect in rock-salt obtained by Rasetti reveals the existence of nine distinct Raman lines both on the Stokes as well as on the antistokes sides. The frequency shifts of these lines have been estimated. From the microphotometer record reproduced in Rasetti's paper, the relative intensities of the lines as well as the intensity ratios of the Stokes to the antistokes lines have also been evaluated. These nine frequencies have been identified as due to the nine distinct modes of vibration of the sodium chloride lattice to be expected on the basis of the Raman dynamics of crystal lattices. Though these vibrations are forbidden in the Raman effect as fundamentals, they are allowed as octaves and appear as such in the spectrum. It is pointed out that the Born theory of crystal dynamics is not capable of offering any satisfactory explanation for the observed facts.

REFERENCES

- | | |
|-------------------------------|--|
| Bhagavantam and Venkatarayudu | <i>Proc. Ind. Acad. Sci. (A)</i> , 1939, 9 , 224. |
| Chelam | .. <i>Ibid.</i> , 1943, 18 , 257. |
| Fermi | .. <i>Moleküle und Kristalle</i> , 1938. |
| ——— and Rasetti | .. <i>Zeit. f. Phys.</i> , 1941, 71 , 689. |
| Pant | .. <i>Proc. Ind. Acad. Sci. (A)</i> , 1943, 18 , 309. |
| Placzek | .. <i>Marx-Handbuch der Radiologie</i> , Vol. VI, Part 2, 1934. |
| Raman | .. <i>Trans. Farad. Soc.</i> , 1929, 25 , 781 ; <i>Proc. Ind. Acad. Sci. (A)</i> , 1941, 14 , 459 ; 1943, 18 , 237. |
| Rasetti | .. <i>Phys. Rev.</i> , 1929, 34 , 367 ; <i>Zeit. f. Phys.</i> , 1930, 61 , 598 ; <i>Nature (London)</i> , 1931, 127 , 626 ; <i>Nuovo Cimento</i> , 1932, 9 , 72. |
| Rutherford | .. <i>Proc. Roy. Soc.</i> , 1931, 130 , 239. |
| Schæfer | .. <i>Zeit. f. Phys.</i> , 1929, 54 , 153. |

LUMINESCENCE SPECTRA AND VIBRATIONS IN CRYSTAL LATTICES

BY D. D. PANT

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 13, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

AN extensive literature¹ has grown up on fluorescence spectra, and numerous studies of the spectra of crystals have been made in the last few years. Cooling the crystals to low temperatures (*e.g.*, that of liquid air or hydrogen) has played a great and fundamental role in these investigations. Luminescence spectra are often diffuse and blurred at ordinary temperatures, and this is usually ascribed to fluctuations in the strength of the crystalline field arising from thermal and other disturbances. On reducing the temperature, these disturbances diminish and the spectra undergo notable changes, in many cases becoming clearly resolved into narrow bands or sharp lines. Analogous changes also occur in the complementary absorption spectra when the temperature is lowered. Hence, it is usually quite essential that the luminescence and absorption spectra should be studied at the lowest available temperatures. Another important fact, as pointed out by Randall,² is that many ordinarily non-fluorescent solids become fluorescent at low temperatures. The belief that only a few substances fluoresce has been proved to be not quite correct, and we know to-day a fairly large number of solids giving luminescence spectra. They may, broadly speaking, be placed in one or the other of two classes.^{3,4} To one class belong the uranyl salts, the platinocyanides, the rare-earth and manganese salts which fluoresce in the pure state due to the presence of an incomplete $3d$ or $4f$ shell. In the other class, the luminescence is due to the presence of impurities, as Boisbaudron⁵ first pointed out, or to some internal distortion or mosaic structure in the crystal. This includes the Lenard-Klatt sulphides, alkali halides, zinc sulphide, chromium and rare-earth activated solids and diamond. The common activating impurities are Cu, Mn, Ag, Bi, Cr, Th and the rare-earth elements. In some cases the stoichiometric excess of the metal (*e.g.*, in zinc oxide and the alkali halides) or exposure to X-rays also produces luminescence.

It is now well known that sharp emission spectra are not the characteristic of gases only. In fact, some polyatomic molecules give continuous

spectra in emission, while the luminescence spectra of some solids give lines as sharp as those of gaseous atoms. As Spedding⁶ has pointed out, we may divide the luminescence spectra of solids into two large classes, the "continuous" and the 'discrete' or 'line' spectra. Spedding has also discussed the origin of these two types. The appearance of clearly resolved lines obviously demands that both the upper and lower states are sharp. The following solids have been known to give discrete or line spectra at sufficiently low temperatures.

1. Diamond where the luminescence is probably due to some sort of mosaic structure.⁷
2. The chromium (transition element) activated luminescent solids, *e.g.*, ruby.
3. Solids containing rare-earth elements.
4. Solids containing foreign atoms scattered through their lattices *e.g.*, the sulphide, halide and oxide phosphors, of some metals.
5. Some pure salts, *e.g.*, the uranyl compounds.
6. Organic compounds having a double bond, *e.g.*, solid benzene.
7. Solidified gases, *e.g.*, solid nitrogen.

Whether the luminescent substances are pure or impurity-activated, the importance of studying their spectra along with the complementary absorption spectra cannot be over-emphasised. At the present moment when the exploration of the energy levels of crystals is making rapid progress, such studies are of great value. Their importance is as great to-day for the understanding of the energy levels in a crystal as was the study of the band spectra of molecules, twenty years ago, to understand the energy levels in the gaseous state. The theoretical side, which has also made a considerable progress within the last thirteen years notably at the hands of Brillouin, Wilson, Peierls, Wigner, Seitz, Slater, Gurney, Mott and others, has been shaped to what is known as the "Zone theory" of the solids. Although this theory claims successfully to have explained the difference between a conductor and an insulator, yet as regards the excited states it has not been very successful. Attempts have been made to apply the theory to the case of luminescence in solids. Thus, Seitz⁹ explains the fluorescence of zinc sulphide and alkali halide phosphors activated by thallium, while Milner¹⁰ gives a broad outline of the difference between the pure and impurity-activated phosphors. It must be said, however, that there is, as yet, no universal mechanism known explaining the observed facts.

Still, whatever may be the mechanism of the main electronic transition, in many cases where this transition is modified by the internal vibrations

of the solid, some very important information can be procured concerning the nature of these vibrations. Such information has become of great interest in view of the recent theory put forward by Raman¹¹ which suggests that the thermal vibrations of the crystals are monochromatic and not continuous, as the theories of Born and Debye assume them to be. Although the Raman scattering of light in crystals usually gives some of the desired information, owing to the selection rules involved, not all the frequencies can appear as fundamentals in every case. In the present paper, an attempt is done to throw some light on the problem from the evidence gained from the literature on the luminescence spectra of solids. Wherever possible this evidence is supplemented by that gained from the corresponding absorption spectra.

2. *Diamond*

This case is of exceptional interest in view of the elementary character of the substance and the simplicity of its structure. The emission of light by diamond in various circumstances has long been familiar knowledge. Crookes and Becquerel who studied the phenomenon noticed and recorded the appearance of some lines in the green and yellow regions of the spectrum. Walter had noticed that some diamonds exhibit an absorption band at 4157 Å. That a bright band appears at the same position in the luminescence of many diamonds was noticed by Ramaswamy,¹² Bhagavantam,¹³ John¹⁴ and by Robertson, Fox and Martin.¹⁵ The subject has since been thoroughly investigated with the diamonds in the collection of Sir C. V. Raman by Nayar¹⁶ and more recently also by (Miss) Anna Mani (1942-43) in her as yet unpublished work. By studying the phenomena at liquid-air temperatures a notable advance has been achieved in the knowledge of the spectra of diamond.

At low temperatures, the 4157 Å band shifts and appears as a sharp line or doublet centred at 4152 Å. The bright green luminescence of some diamonds is similarly associated with a sharp line at 5032 Å. The appearance of bright and dark lines with these wave-lengths respectively in emission and in absorption indicates that they represent electronic transitions. Their intensities vary enormously from diamond to diamond. These electronic transitions are found further to be associated with emission spectra showing much observable detail and extending towards longer wave-lengths in fluorescence; similar spectra extending towards shorter wave-lengths are also noticed in absorption in each case. The intensities of these spectra vary in the same way and proportionately with that of the associated electronic transition from specimen to specimen. The features observed in emission and absorption are found to exhibit

perfect mirror-image symmetry in the frequency scale with reference to the associated electronic transitions. These facts indicate that the spectra arise from combinations of crystal lattice vibrations with the electronic transitions. The observed frequency differences lie in the infra-red region of the spectrum, and the values determined from emission and absorption data agree with each other and are also the same for both the blue and the green luminescence.

The most clearly defined and accurately measurable lattice frequencies for diamond found in the studies of Nayar and of (Miss) Mani are (in wave-numbers) 1332, 1248, 1149, 1088, 1013, 935, 784 and 544, and these are probably the eight fundamental frequencies of the diamond lattice. The spectra indeed extend to both larger and smaller frequency shifts from the electronic transitions. They are, however, both feeble and diffuse towards larger frequency shifts, indicating that these are probably octaves and combinations of the frequencies listed above. Much detail is also observable and measurable in the spectral region with frequency shifts smaller than 544 cm^{-1} . This region appears only feebly with the 4152 transition, but quite strongly with the 5032 transition. It is noteworthy that the highest fundamental frequency 1332 determined from these studies agrees closely with the characteristic frequency of diamond observed in its Raman spectrum. Taken altogether, the results make it clear that the vibration spectrum of the diamond lattice consists essentially of a series of discrete monochromatic frequencies and is not a continuous one.

3. Chromium (Transition Elements) as Activator

Most of the divalent manganese and trivalent chromium compounds give well-defined spectra. The electronic transition responsible for these is due to the rearrangement of the electrons in the incomplete $3d$ shell. Manganese happens to be the best impurity activator inasmuch as it imparts luminescence to the greatest number of cases. Randall¹⁷ has studied the fluorescence spectra of pure manganese halides and also of the compounds activated by manganese. Kroger¹⁸ has studied the Zn_2SiO_4 , Mn_2SiO_4 mixed system. Considerations of the absorption spectra of the pure compounds of manganese by Gielessen²¹ show that the electronic transition is ${}^2\text{G} - {}^4\text{F}$ of the Mn^{++} ion. No associations of the lattice vibrations with the electronic transition seem to have been recorded.

Deutschbein¹⁹ has studied the chromium activated phosphors most extensively. Like chromium, the cobalt and nickel phosphors also give sharp lines both in fluorescence and absorption. It is found that chromium fluoresces in compounds where Cr_2O_3 can be isomorphous with the

bedding, *e.g.*, in ruby. Where the distortion of the lattice is greater, the spectra are more diffuse. Out of the many naturally occurring stones such as the ruby, sapphire, red spinel, etc., which emit the red fluorescence of the chromium impurity,²⁰ ruby has been studied most thoroughly. It is suggested that the fluorescent doublet at $\lambda\lambda$ 6927 and 6942 Å° is due to the Cr⁺⁺⁺ ion. Among the recent workers who have studied the fluorescence spectrum of ruby may be mentioned Venkateswaran,²² Thosar²³ and Miss Mani.²⁴

Apart from the electronic transition in Cr⁺⁺⁺ ion, the part played by matrix crystal corundum has to be considered. Deutschbein was the first to explain the sharp band at λ 7138 Å° ($\nu = 14006$ cm.⁻¹) as being due to the superposition of the Raman frequency 412 cm.⁻¹ of the ruby lattice on the electronic transition responsible for the band at λ 6935 Å° (14416 cm.⁻¹). Thosar who suggested that the Cr⁺⁺⁺ ion replace the Al⁺⁺⁺ ion in the lattice was led to the conclusion that bands on the antistokes side of the main band must be due to the proper vibrational frequencies of the molecular group Cr₂O₃. (Miss) Mani has studied the luminescence, Raman scattering and absorption of ruby, and she finds that there is an approximate mirror-image symmetry for the bands at $\lambda\lambda$ 6595, 6693 and 6817 Å on the antistokes side and for those at $\lambda\lambda$ 7324, 7275, 7188, 7138 and 7030 on the Stokes side. With the help of three infra-red frequencies at 909, 847 and 741 cm.⁻¹ and two Raman frequencies at 412 cm.⁻¹ and 376 cm.⁻¹ of the Al₂O₃ lattice, she has suggested that 8 bands both on the Stokes and antistokes side could be explained.

In this connection it is worthwhile mentioning certain features of the absorption spectra of chrome-alums which have been studied by various investigators²⁵⁻²⁹ at temperatures as low as that of liquid hydrogen. Sauer has for example studied the effect of isomorphous replacement in a group of eleven sulphate and selenate chrome alums at -190° C. Discrete absorption is found in general in the red and orange region followed by a strong continuum with maxima approximately at $\lambda\lambda$ 5700 and 4000 Å°. On lowering the temperature to that of liquid hydrogen, the continuum narrows, becomes less diffuse and often resolves into finer structure. The spectra of selenates are richer in lines than those of potassium chromium sulphate and the lines are superior in sharpness at the temperature of liquid air. Krauss and Nutting have analysed the spectra consisting of a number of lines, and they find that combinations of lattice vibrations with both upper and lower electronic states of Cr⁺⁺⁺ are involved. Bands are observed in all the alums shifted about 330, 570 and 800 cm.⁻¹ to higher frequencies than the electronic absorption lines. Combinations of the internal oscillations of the anions are weak but have also been observed.

Here again we find definite evidence regarding the sharpness of the internal vibrations in the solid state.

4. *The Rare-Earth Phosphors*

The ions of rare-earths, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm give very sharp lines both in the absorption and luminiscence spectra. Such spectra are found both in the pure rare-earth salts and the solids where they are present as impurities. The lines are sharper than those obtained in the chromium activated phosphors. It is found that unlike the Cr^{+++} ion the rare-earth ions need not be isomorphous with the bedding. The spectra arise out of the transition within the shielded incomplete $4f$ shell of the ion. The levels are split up by the electric fields within the atom in accordance with the theory of Bethe.³⁰ Each line has therefore, companions depending on the symmetry of the crystalline field and J values of the states of the ion.

The naturally occurring fluorites were studied by Haberlandt³¹ and his co-workers who recognised that the divalent rare-earth ions are responsible for the fluorescence. The pioneering work in the luminescence spectra of the rare-earths was, however, done by Tomaschek³² and collaborators. The sharpness of the lines which resembles that of the lines in the gaseous state permits to study the influence of the surrounding field on the spectra very accurately. At Dresden a most thorough investigation of the problem has been made by what they call 'the method of line fluorescence'. Extremely useful results have been obtained regarding the nature of the crystalline fields, structure of glasses, phosphorescence centres in glasses, the hyperstructure of the crystallised substances and the constitution of liquid solutions which have been shown to have crystalline structure. It is found that the line structure of the spectra in the crystalline state is diffuse in the vitreous state. Fluorescence of the pure salts and their solutions has also been studied^{33, 34} and recently Chatterji³⁵ has given the interpretation of the fluorescence spectra of artificial fluorites activated by the rare earth elements.

Tomaschek³⁶ has discussed the known facts regarding the line spectra of solid solutions in emission and absorption, particularly those of the rare earths in a separate paper. According to him the spectra represent electronic jumps on which are superposed the vibrations of the parent lattice and the light centre itself. The vibrations thus obtained are of lower frequencies than those obtained from the Raman effect of the parent lattice. This difference is explained on the assumption that the rare-earth molecules may act as inert loads. If this explanation is correct the changes of frequency should be greater the larger the rare-earth and smaller the bedding molecule. This point has been experimentally confirmed. For example, the praseodymium

ion which produces a greater change of frequency than the samarium ion has a diameter 3 per cent. greater than that of the latter. On the other hand, barium oxide has a larger diameter than calcium oxide and the change of frequency produced by bedding samarium in it is much less. Diagrams are given by Tomaschek to show how the lattice frequencies of alkaline earth sulphides and oxides compare with those obtained from the fluorescence spectra when samarium and praseodymium are embedded in them. Tomaschek has further shown that similar lattices give similar spectra and that crystal type has a great influence on them. Leaving aside the mechanism of electronic transition, the position can be summed up by saying that frequencies characteristic of the matrix lattice modified by the presence of the rare-earth ion in question are found in the spectra of rare earth phosphors. These frequencies are associated with the electronic transition in the ion and surely, there cannot be the least doubt about the monochromatism of these lines.

In the following, the foregoing remarks will be supplemented with evidence gained from the experiments on the absorption spectra of some crystalline rare-earth salts. These spectra again consist of sharply defined and widely spaced groups of bands. The separate groups owe their origin to the decomposed multiplet levels by the electric fields. The electronic transition again arises out of the rearrangement within the 4f configuration of the rare-earth ion.³⁷ A good amount of work has been done by Spedding³⁸ and others who find that low lying levels (electronic) are to be observed in $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$; $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and the europium salts. But to account for the large number of lines it is necessary to couple internal vibrations of the crystal with the electronic transition. The work of Ewald,³⁹ Howe and Herbert⁴⁰ and Weissman and Freed,⁴¹ however, demands greater attention here, for it gives some definite evidence regarding the vibrations in the rare-earth crystals.

Taking very thick layers of neodymium salts Ewald found that each group of electronic transitions is accompanied by faint lines, spaced in the same manner on the short wave-length side. The spacing in the weak lines is found to be the same in each group. In the case of the mixed nitrate $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{Nd}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ these frequencies correspond to the vibrations of the NO_3^- ion and the H_2O molecule. On replacing the water of crystallisation by heavy water, vibrations corresponding to that of D_2O are observed. Ewald also found that some low frequencies from 50 cm^{-1} to 200 cm^{-1} represented lattice vibrations; for an increase in the mass of the lattice atoms effected a decrease in the frequencies. Hellwege⁴² by the *restrahlen* method found that these were actually the crystal oscillations,

Striking results are obtained by Freed and Weissman in the corresponding salt of europium. The spectrum, remarkably enough, consists of sharp lines even at room temperatures. They also find that in addition to the lattice oscillations on the short wave-length side of the electronic frequency, there appears a similar pattern of lines towards the longer wave-lengths displaced by an equal amount in frequency. On lowering the temperature, these new lines vanish; thus indicating that they are thermal oscillations of the lattice and that their presence in the spectrum corresponds to the anti-stokes frequencies in Raman effect. These authors also give evidence to show that crystal structure continues even in the solution state of the salt. But the lines are naturally more diffuse there.

The observations of Weissman and Freed appear to have a great significance from our point of view. The results show that the vibrations of the solids are (at least in the observed case) sharp even at room temperatures. It seems plausible that the diffuseness in any observed spectra is mainly due to the electronic transition, the thermal vibrations remaining still sharp.

5. Fluorescence Spectra of Impurity Activated Solids

A greater number of solids fluoresce only in the impure state. The chief characteristic of their luminescence spectra is the lack of resolution even at low temperatures. On this account, nothing much has been said from the theoretical point of view. The alkali halide phosphors have been studied by a number of investigators, notably by Pohl, Hilsch and others.⁴³ The absorption bands by which luminescence may be stimulated, consist of several sharp peaks near λ 3000 Å to the short wave-length side and are characteristic of such phosphors. They are, however, absent in the pure halides. The luminescence lies in the near ultra-violet and visible region. Von Hippel⁴⁴ has given a theory of these phosphors. Zinc sulphides give broad bands depending on the nature of the impurity atoms.⁴⁵ Reference to Seitz's theoretical discussion in this connection has already been made.

From the experimental standpoint the resolution of the broad, featureless bands in many impurity activated phosphors has been attempted by Schmidt,⁴⁶ Schellenberg⁴⁷ and Howes⁴⁸ but much success has not been obtained. Recently, however, Ewles³ has done some valuable work in this direction and here, his results will mainly be quoted. He obtained the most remarkable resolution of the ultra-violet bands of CaO phosphors, into almost line-like components with cathode ray excitation. This condition was obtained by cutting down the cathode ray current to a fraction of a micro-ampere by running the machine very slowly or by putting a spark gap in parallel with the tube. The spectrum obtained in the ultra-violet

region appears to be divided into a number of groups of broadened lines each suggesting a band group. The bands in the visible region are however broad.

In CaO, for example, two groups of bands are observed. They are named as (F, G) and (H, K, L) groups. The bands can be represented by a formula of the type

$$\nu = \nu_e + (v' + \frac{1}{2}) \omega' - (v'' + \frac{1}{2}) \omega''.$$

The following table gives the bands of the (F, G) group.

TABLE I
Bands in the F, G Group of CaO

Designation	Observed	Calculated	ν', ν''
F	27404	27404	0, 0
G	27166	27160	1, 1
F ₁	26891	26896	0, 1
G ₁	26647	26652	1, 2
F ₂	26385	26388	0, 2
G ₂	26142	26144	1, 3
F ₃	25886	25880	0, 3

$\nu_e = 27526$ corresponds to the electronic transition:

CaI $4s4p \ 3P^o - 4s \ 4d \ ^3D$, $\omega' = 244 \text{ cm.}^{-1}$ and $\omega'' = 508 \text{ cm.}^{-1}$ Similarly for the (H, K, L) group $\nu_e = 25816$, and $\omega' = 294 \text{ cm.}^{-1}$ and $\omega'' = 493 \text{ cm.}^{-1}$

The frequencies 508 cm.^{-1} and 493 cm.^{-1} are presumably the same as 453 cm.^{-1} the maximum vibrational frequency of the CaO lattice as given by Tolksdorf.⁴⁹ Further evidence that the CaO crystal plays a predominant part in the emission of the (H, K, L) group is given in favour of this assumption.

Fourteen samples of CaO phosphors, one pure and 13 impurity activated have been examined both with cathode ray and ultra-violet excitation. It appears that the activators merely determine the relative intensities of a set of groups but the positions are determined by the lattice itself. The results obtained with CaO are confirmed by working with other sulphides and oxides. In the case of SrO a set of 4 broadened lines is obtained which can be put in the equation,

$$\nu = 26410 + (v' + \frac{1}{2}) \omega' + (v'' + \frac{1}{2}) 404 \text{ cm.}^{-1}$$

For ZnO, similarly,

$$\nu = 26764 + (v' + \frac{1}{2}) 322 + (v'' + \frac{1}{2}) 571 \text{ cm.}^{-1}$$

The frequencies 404 cm.^{-1} and 322 cm.^{-1} are probably due to the SrO and ZnO lattices. The results of other previous workers have been explained on similar lines. Although the evidence regarding the part played by the

crystal frequencies is not very conclusive, the review shows that, at the liquid-air temperature, well resolved, broadened lines presumably due to the lattice vibrations have been obtained. It would be of interest to study these spectra at temperatures even lower than this. Even here, it is highly interesting to note that the spectra which previously were known to consist of broad featureless bands have been resolved into line-like appearance.

6. The Uranyl Compounds

It is well to emphasise the dependence of luminescence spectra on crystal structure.⁵⁰ The uranyl salts and the platinocyanides, which are two striking examples of complex co-ordination groups, greatly owe their property of luminescence to the crystalline state. Levy,⁵¹ for example, found that out of the three pure samples of $\text{Ba Pt (CN)}_4\text{H}_2\text{O}$ only two, which were crystalline, gave fluorescence. In uranyl compounds also, Nichols and Howes⁵² find that the characteristic spectra can only be obtained in the crystalline state. Even in substances where uranium acts as impurity activator, well-resolved spectra at liquid-air temperatures have been obtained only if the matrix substance is in the crystalline form.⁵³ It is interesting to see that the fluorescence study of uranyl compounds in the crystalline state gives much information regarding the nature of vibrations in the solid.

Fluorescence is the property of uranyl compounds only; the uranium salts do not show any luminescence. At room temperatures, the pure salts fluoresce giving rise to nearly 8 rather broad and diffuse regularly spaced bands in the green-red region. These become sharp and get resolved into lines at the liquid-air temperature. At the liquid hydrogen temperature the lines have been reported to become as fine as those of a spark spectrum. Table II gives the wave-number values of the lines in the fluorescence spectrum of uranyl fluoride at the liquid air temperature taken by Mr. N. D. Sakhwalkar in this laboratory.

TABLE II
The fluorescence Lines in $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$

Series	Group					$\Delta \nu$ (average)
	1	2	3	4	5	
A	20237 (w)	19360 (d)	18503 (d)	17641 (w)		865 cm^{-1}
B	20083 (s)	19218 (s)	18354 (s)	17493 (m)	16740 (w)	861 cm^{-1}
C		19152 (d)	18293 (d)	17429 (m)	16577 (m)	858 cm^{-1}
D		19126 (d)	18270 (w)			856 cm^{-1}

s = strong
m = medium

d = dim
w = weak

This is the simplest fluorescence spectrum to be found in the uranyl salts. Measurement of the lines is very approximate; still it will be seen that the spectrum consists of 5 groups each separated from the next one by 860 cm^{-1} . This separation of 860 cm^{-1} is characteristic of all the spectra. Dieke and Van Heel,⁵⁴ therefore, suggested that the electronic transition is due to the uranyl ion and that the jump is modified by the oscillation frequency 860 cm^{-1} of the UO_2 group. Van Heel⁵⁵ drew up the energy level diagrams to explain the spectrum, but a really satisfactory explanation has not yet come forward.

The Raman spectra of the UO_2^{++} ion in solution were obtained by Conn and Wu⁵⁶ and Satyanarayana.⁵⁷ It is confirmed that the 860 cm^{-1} frequency is due to the symmetric ($\text{U}=\text{O}$) vibration. Two more frequencies at 930^* cm^{-1} and 210 cm^{-1} correspond to the antisymmetric and the deformational vibrations of the bent UO_2^{++} molecule. In addition to these, certain companions of these vibrations have also been obtained which are due to the undissociated uranyl compound. Taking these facts into account and treating UO_2^{++} molecule as a triangular one, the author has found it possible to explain the spectra more or less completely with due regard to the intensities of component lines of each groups.

The absorption spectra again consist of sharp bands spaced at intervals of 700 cm^{-1} . This is obviously the vibrational frequency in the excited state of the uranyl ion corresponding to 860 symmetric valence vibration of the ground state. Thus, the uranyl ion, as far as the vibrational energies are concerned, behaves more or less as a free gaseous molecule in the crystalline uranyl compounds and gives rise to extremely sharp bands in the luminescence spectra which are mostly due to the vibrations of the ion.

1. Solid Benzene

Investigations of the Raman spectra of crystals probably first revealed the sharpness of the infra-red vibrations; attention to this was drawn as early as 1929.⁵⁸ Some solids such as ice, salts having SO_4^{--} , NO_3^- , *etc.*, as radicals show, that vibrations corresponding to the molecule or the radical in question do exist in the solid. The luminescence and absorption spectra which have been described above show that similar vibrations exist in the luminescent solids and are as sharp and discrete as in the gaseous state. Some more evidence obtained from the study of fluorescence and absorption of C_6H_6 will now be given to show that vibrations corresponding to the gaseous state also present themselves in the solid state.

* Observed in the infra-red absorption spectrum of the uranyl salts in crystalline state by Conn and Wu.

The fluorescence spectrum of benzene has been investigated both in the gaseous⁵⁹ and the solid state.⁶⁰ The fluorescence spectrum of solid benzene at -185°C . consists of two progressions F, E, D, C, B and *e, d, c, b*. The interval between F-E or *e-d* is 990 cm^{-1} and that between *e-E* is $\sim 600\text{ cm}^{-1}$. These bands become extremely sharp at the liquid hydrogen temperature. For, the structure of the bands, instead of splitting up, completely disappears at this low temperature and only the maxima are left. It is remarkable that the fluorescence spectrum of the solid benzene closely agrees with series II fluorescence progression of the vapour state (Table III). The equation for this series is given as $\nu = 39000 - 1000n - 163p$.

TABLE III
Fluorescence Spectra of Solid and Gaseous Benzene

$\begin{array}{c} n \\ p \end{array}$	2		3		4		5		6	
	Vapour	Solid	Vapour	Solid	Vapour	Solid	Vapour	Solid	Vapour	Solid
0	2675		2749		2825	2822	2907	2904	2996	
1	2686	2686	2759	2756	2838	2834	2920	2921	3007	3008
2	2698	2695	2772	2772	2851	2853	2933	2935		
3	2710	2712	2785	2785	2864	2868	2948 2950	2956	3038	

The absorption spectra of benzene and the substituted benzenes have also been studied both in the vapour state⁶¹ and solid states.⁶⁰ Due to the great advance achieved in the understanding of the polyatomic spectra in recent years, it has been possible to give a rather complete explanation of the observed absorption spectrum of benzene.⁶² The solid benzene at -180°C . shows the presence of very strong progression, with a spacing of 923 cm^{-1} in the spectrum. This is similar to that observed in the gaseous state. The weaker progression of the gaseous benzene with a spacing of 505 cm^{-1} is, however, absent in the spectrum of the solid benzene. The latter is again shifted by 261 cm^{-1} to the red. A complete explanation for the observed bands has been given except for some weaker bands spaced at intervals of nearly 60 cm^{-1} which are probably due to the superposition of the crystal frequencies. For, they cannot be due to the rotational energy which will not exist at such low temperatures.

It will be noted that the frequencies 990 cm^{-1} and 922 cm^{-1} are the totally symmetric vibration frequencies of the C-C bond in the ground and the excited states. This case is exactly similar to that already mentioned in the case of uranyl compounds. The 606 cm^{-1} and 520 cm^{-1} again are the C vibrational frequencies in the ground and the excited states.

It is not necessary to give a further account of the fluorescence and absorption spectra of other organic molecules. It is known that an unsaturated or resonating band in organic compounds generally gives rise to discrete spectra. For, when a double bond exists, one of the electrons can be excited without destroying the bond and this accounts for the sharp levels.

8. Solid Nitrogen

In 1924 Vegard⁶³ discovered that when solid nitrogen was bombarded by cathode rays it emitted a radiation, the spectrum of which consisted of sharp bands and lines. He extended his work considerably and the spectra of solid nitrogen, nitrogen-argon mixtures in various proportions and so on, at the temperatures of liquid hydrogen and helium, were studied by various types of excitations, *e.g.*, slow and swift cathode rays, canal rays, X-rays etc.⁶⁴ A considerable number of spectra were thus studied and the numerous lines and bands were classified into series and systems of such series. It is not possible to give all the details regarding these; in brief it may be said that they can be represented by equations of the type

$$\text{e.g., } \nu_{\delta} = 21245.5 - 1631.1n + 10.7n^2$$

$$\nu_{\theta} = 22976.1 - 1633.1n + 11.3n^2$$

for the δ and the θ series respectively. Other types of series which are characteristic of the solid state (for they appear in the phosphorescence emission) can be represented similarly but the spacing between the successive bands is larger here,

$$\text{e.g., } \nu_{\xi} = 17232 + 2231.5n + 7.4n^2.$$

Series D, α , χ , ξ and ϵ are similar so far as the spacing between the successive bands is concerned. The nature of the equations clearly shows that the series are due to an electronic transition modified by a vibrational frequency which combines with it in various quanta. The ϵ series which is of greatest importance, involves vibrational frequencies of the excited as well as the ground states of the electronic transition.

Thus,

$$\epsilon(m_1, m_2) = \nu_0 + T_2(m_2) - T_1(m_1)$$

where m_1 , m_2 correspond to the upper and the lower levels of the crystal. T_2 and T_1 are approximately vibrational frequencies of the excited and the ground states respectively; for $T_2(m_2) = 1453.1 m_2 - 14.866 m_2^2$ and $T_1(m_1) = 2323.3 m_1 - 14.898 m_1^2$.

Experiments showed that the solid nitrogen has two allotropic modifications; the α -form which exists below 35.5° K. and the β -form which

exists above this transition point. While both the forms give luminescence on excitation with the cathode rays, it is only the α -form that gives the after-glow (phosphorescence). The D, α , χ , ξ and ϵ series which appear in the after-glow spectrum are thus the typical bands of the solid form. Vegard explained the non-appearance of the after-glow in the β -form by assuming that the electronic transition, which is a forbidden one, appears in the α -form because the molecular axes are fixed in the lattice (which is cubic).⁶⁵ In the β -form, however, the axes are absent because the molecule rotates.⁶⁶ This, however, does not explain the decaying property of the after-glow which does not obey the exponential law. It was, therefore, assumed that the bombarding rays produce dissociation of the molecules into atoms. The latter recombine to form an excited molecule by the force of some chemical energy.

The then existing facts were all in agreement with the assumption that the electronic transition is of the forbidden type. The level $A^3\Sigma$ of the N_2 molecule was known to exist from the analysis of the first positive nitrogen bands. This level is metastable with respect to the ground $X^1\Sigma_g^+$ state. The vibrational levels of the ground and the excited states were known to be of the values of 2359.6 cm^{-1} and 1460.4 cm^{-1} ⁶⁷ respectively. However, the discovery of the Vegard-Kaplan bands of N_2 by Kaplan⁶⁸ (transition $A^3\Sigma_u^+ - X^1\Sigma_g^+$) completely removed the last traces of doubt. The ϵ bands now correspond to the above transition⁶⁹ and vibrational energies T_1 and T_2 correspond to the vibrational frequencies of the $^1\Sigma^+$ and $^3\Sigma$ states respectively.

Lastly, Vegard finds that the series are not composed of single lines but of two or more components. The splitting up is more pronounced at the liquid helium temperature than at that of liquid hydrogen. The multiplicity cannot be due to the rotational energy for obvious reasons. Excepting for the α -series which has a splitting of 69 cm^{-1} other series show a difference of 40 cm^{-1} between the successive components. Vegard suggests that these are due to the change of vibrational energy of the molecular element in the crystal lattice.⁷⁰ In other words, these are the oscillation frequencies of the lattice.

Here again we have strong evidence to show that thermal frequencies existing in the solid state are sharp and monochromatic. Further, it has once again been shown that the vibrational energy of the molecule remains more or less the same both as regards monochromatism and frequency in the gaseous and the solid states. A little difference, if at all, has to be expected due to the Van der Waals forces.

Summary

A general survey of the known luminescence spectra of crystals is given. Those which give discrete spectra have been divided into seven classes. The luminescence spectrum of each of these crystals is examined to see what evidence it gives regarding the nature of the vibrations in the crystal lattices. Wherever possible the information thus obtained is supplemented by the evidence furnished by the complementary absorption spectra. It is shown that there is a mass of striking evidence indicating that vibrational frequencies are sharp and monochromatic in all crystals. Those luminescence spectra, which are not discrete are due to an electronic transition in which one or both the electronic states involved are not sharp and hence no evidence regarding the vibrational frequencies can be gained from them. It is remarkable that over the whole range of crystal structure—from the typical covalent crystal diamond to the typical Van der Waals crystal solid nitrogen—the vibrational frequencies are all sharp and monochromatic. The ionic crystals, *e.g.*, the uranyl salts are also no exception to this rule. In many crystals some of the constituents, *e.g.*, N_2 in solid nitrogen, C_6H_6 in solid benzene, the UO_2^{++} molecule in uranyl salts and so on, behave as if they are in the gaseous state. For example, the vibrational frequency observed in the fluorescence spectrum of solid benzene at very low temperatures is thus the same as that of the ground state of the C_6H_6 molecule, probably the only difference being that the observed bands are more discrete in the crystal state owing to the absence of the rotational lines.

REFERENCES

1. Pringsheim .. *Fluoreszenz und Phosphoreszenz*, Berlin, 1928.
Hirschlaff .. *Fluorescence and Phosphorescence*, Metheun, 1938.
Baly .. *Spectroscopy*, Vol. II, 1927, 234.
Curie .. *Luminescence des corps solides*, Paris, 1934.
Perrin .. *Fluorescence*, Paris, 1931.
 Acta Physica Polonica, 1936, 5, 1-431.
 Trans. Farad. Soc., 1939, 35, 1-238.
2. Randall .. *Nature*, 1938, 142, 113 ; *Trans. Farad. Soc.*, 1939, 35, 2.
3. Ewles .. *Proc. Leeds Phil. Soc.*, 1935-40, 3, 277 and 416 ; *Proc. Roy. Soc.*, 1938, 167, 34.
4. Randall and Wilkins .. *Reports on Progress in Physics*, 1939, 6, 174.
5. Boisbaudron .. *Compt. Rend.*, 1886, 103, 468.
6. Spedding .. *Trans. Farad. Soc.*, 1939, 35, 65.
7. Raman, Sir C. V. .. *Current Science*, 1943, 12, 33.

8. Seitz .. *Modern Theory of Solids*, McGraw Hill Book Company, 1940.
- Gurney and Mott .. *Electronic Processes in Ionic Crystals*, Oxford Univ. Press, 1940.
9. Seitz .. *J. Chem. Phys.*, 1938, 6, 150 ; *Trans. Farad. Soc.*, 1939, 35, 74.
10. Milner .. *Trans. Farad. Soc.*, 1939, 35, 101.
- See also
- Johnson .. *J. O. S. A.*, 1939, 29, 387.
11. Raman, Sir C. V. .. *Proc. Ind. Acad. Sci.*, 1941, 14, 459.
12. Ramaswamy .. *Ind. J. Phys.*, 1930, 5, 97.
13. Bhagavantam .. *Ibid.*, 1931, 5, 169 and 573.
14. John .. *Ibid.*, 1931, 6, 305.
15. Robertson, Fox and Martin *Phil. Trans. Roy. Soc.*, 1934, 232, 494.
16. Nayar .. *Proc. Ind. Acad. Sci.*, 1941, 13, 483 ; 1941, 13, 534 ; 1941, 14, 1 ; 1942, 15, 293.
17. Randøll .. *Proc. Roy. Soc.*, 1939, 170, 272.
18. Kröger .. *Physica*, 1939, 6, 764.
19. Deutschbein .. *Ann. d. Physik*, 1932, 14, 713 ; 1934, 20, 828 ; *Phy. Zeits.*, 1932, 33, 874.
20. Candler .. *Atomic Spectra*, Vol. II, 1937, Camb. Univ. Press.
21. Gielessen .. *Ann. d. Phy.*, 1935, 22, 537.
22. Venkateswaran .. *Proc. Ind. Acad. Sci.*, 1935, 5, 459.
23. Thosar .. *Phil. Mag.*, 1938, 26, 878 and 380.
24. Anna Mani (Miss) .. *Proc. Ind. Acad. Sci.*, 1942, 15, 52.
25. Schnetzler .. *Ann. d. Phy.*, 1931, 10, 373.
26. Snow and Rawlins .. *Proc. Camb. Phil. Soc.*, 1932, 28, 522.
27. Sauer .. *Ann. d. Phy.*, 1928, 87, 197.
28. Spedding and Nutting .. *J. Chem. Phys.*, 1934, 2, 421.
29. Krauss and Nutting .. *Ibid.*, 1941, 9, 133.
30. Bethe .. *Ann. d. Phy.*, 1929, 3, 133.
31. Haberlandt, Karlik and Przibram *Akad. wiss Wien Ber.*, 1934, 143, 151, etc.
32. Tomaschek .. *Ann. d. Phy.*, 1927, 84, 329 and 1047.
- and Deutschbein .. *Ibid.*, 1933, 16, 943.
- Gobrecht .. *Ibid.*, 1937, 28, 673.
- Deutschbein and Tomaschek *Ibid.*, 1937, 29, 311.
- Tomaschek and Deutschbein *Glustech Ber.*, 1938, 16, 155.
- Also
- Tomaschek .. *Trans. Farad. Soc.*, 1939, 35, 148.
33. ——— and Mehnert .. *Ann. d. Phy.*, 1937, 29, 306.
34. Deutschbein and Tomaschek *Ibid.*, 1937, 29, 311 and 324.

35. Chatterji .. *Zeit. f. Phy.*, 1939, **113**, 96.
36. Tomaschek .. *Ibid.*, 1932, **33**, 878; see also Tomaschek, *Acta Physica Polonica*, 1936, **5**, 393.
37. Bethe and Spedding .. *Phy. Rev.*, 1937, **52**, 454.
 Gobrecht .. *Ann. d. Phy.*, 1937, **28**, 673.
 Van Vleck .. *J. Phy. Chem.*, 1937, **41**, 67.
 Ellis .. *Phy. Rev.*, 1936, **49**, 875.
 Mukherji .. *Ind. J. Phys.*, 1937, **11**, 123.
38. Spedding, Hamlin and Nutting .. *J. Chem. Phy.*, 1937, **5**, 191.
 Spedding and Hamline .. *Ibid.*, p. 429.
 ———, Howe and Keller .. *Ibid.*, p. 417.
 ———, Moss and Walker .. *Ibid.*, 1940, **8**, 908.
 Freed and Weissman .. *Ibid.*, 1940, **8**, 878.
39. Ewald .. *Ann. d. Phy.*, 1939, **34**, 209.
40. Howe and Herbert .. *J. Chem. Phy.*, 1939, **7**, 277.
41. Weissman and Freed .. *Ibid.*, 1940, **8**, 227 and 840.
 See also
 Freed .. *Rev. Mod. Phy.*, 1942, **14**, 105.
42. Hellwege .. *Zeit. f. Phy.*, 1939, **113**, 192.
43. Hilsch .. *Zeit. f. Phys.*, 1927, **44**, 860; *Proc. Phy. Soc.* (extra part), 1937, **49**, 40.
 Pohl .. *Ibid.*, 1937, **49**, 3, etc.
 See also
 Pringsheim .. *Rev. Mod. Phy.*, 1942, **14**, 132.
44. Hipple .. *Zeit. f. Phy.*, 1936, **101**, 680.
45. See for instance,
 Lenard and Tomaschek .. *Handbuch der exp. Phy.*, 1928, **13**, 1, 2.
46. Schmidt .. *Ann. d. Phy.*, 1932, **12**, 211.
47. Schellenberg .. *Ibid.*, 1932, **13**, 249.
48. Howes .. *Carnegie Inst. Wash. Report*, No. 384, 1928.
49. Tolksdorf .. *Z. Phy. Chem.*, 1928, **132**, 161.
50. Servigne .. *Compt. Rend.*, 1935, **200**, 2015.
 Iwase .. *Inst. Phy. Chem. Research Sci. Paper*, Tokyo, 1935, **561**, 1.
51. Levy .. *J. Rontgen Soc.*, 1916, **12**, 13.
52. Nichols and Howes .. *Corngie, Inst. Wash. Report*, No. 298.
53. ———, Mabel and Slattery .. *J. O. S. A.*, 1926, **449**, 12.
54. Dieke and Van Heel .. *Leiden Communications*, 1925, Suppl. No. 55A.
55. Van Heel .. *Ibid.*, 1925, Suppl. No. 55B.
56. Conn and Wu .. *Trans. Farad. Soc.*, 1938, **34**, 1483.
57. Satyanarayana .. *Proc. Ind. Acad. Sci.*, 1942, **15**, 414.

58. Raman, Sir C. V. .. *Trans. Farad. Soc.*, 1929, **25**, 781.
59. Kistiakowsky and Nells .. *Phy. Rev.*, 1932, **41**, 595.
Cuthbertson and *J. Chem. Phys.*, 1936, **4**, 9.
Kistiakowsky
60. Reimann .. *Ann. d. Phys.*, 1926, **80**, 43.
Pringsheim and .. *Zeit. f. Phys.*, 1926, **40**, 75.
Kronenberger
Kronenberger .. *Ibid.*, 1930, **63**, 494.
See also
Titeica .. *Acta Physica Polonica*, 1936, **5**, 381.
61. For a list, see
Sponer and Teller .. *Rev. Mod. Phys.*, 1941, **13**, 76.
Sklar .. *Ibid.*, 1942, **14**, 232.
62. *E.g.*,
Sponer, Nordheim, Sklar .. *J. Chem. Phys.*, 1939, **7**, 207.
and Teller
63. Vegard .. *Comm. Lab. Leiden*, No. 175.
64. For example, see
Vegard .. *Ann. d. Phys.*, 1926, **79**, 377; *Comm. Lab. Leiden*, No. 183,
200 and supplementary No. 59.
65. ————— .. *Nature*, 1929, **124**, 267 and 337; *Zeit. f. Phys.*, 1928, **58**, 497.
66. ————— .. *Ann. d. Phys.*, 1930, **6**, 487.
67. See
Jevons .. *Report on Band Spectra of Diatomic Molecules*, p. 284.
68. Kaplan .. *Phy. Rev.*, 1934, **45**, 534.
69. Vegard .. *Nature*, 1935, **135**, 1073; 1934, **134**, 697.
70. ————— .. *Ibid.*, 1930, **125**, 14.

CHARACTER TABLES FOR THE ATOMIC VIBRATIONS IN SOME CUBIC CRYSTALS

BY E. V. CHELAM

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

IN an earlier paper in this symposium, a general group-theoretical method for dealing with lattice vibrations has been indicated. It has been shown that the solution of the normal vibration problem depends upon a knowledge of the character tables for some point groups which are associated with the different vectors* of the translation group. In the present paper it is proposed to indicate the applications of that method to four crystals of the cubic system, *viz.*, zincblende, diamond, fluorspar and rock-salt. A complete analysis of the normal modes of these and other crystals has already been given in an earlier paper of this series, basing the discussion on purely intuitive geometric principles. Hence a group-theoretical discussion of simple cases like the vibrations of a simple cubic lattice, simple face-centred lattice, body-centred lattice, etc., is not needed here. To illustrate the principles, we propose here to put down the appropriate character tables and the nature of the normal modes for the four crystals mentioned above. All the cases considered here have a face-centred structure. The eight possible vectors for this case fall into three distinct sets, as is evident by a very simple application of the symmetry operations. The $(1, 1, 1)$ vector forms a set by itself and $(1, -1, -1)$; $(-1, 1, -1)$; $(-1, -1, 1)$ another set. The remaining four vectors, $(-1, -1, -1)$; $(-1, 1, 1)$; $(-1, 1, 1)$ and $(1, 1, -1)$ form a set by themselves and each can be carried over into the others by the symmetry operations. Thus the interesting feature in the face-centred system is that $(-1, -1, -1)$ becomes equivalent to the other three. We now investigate these three cases separately.

2. Rock-salt, Zincblende, Diamond and Fluorspar Lattices

All these cases can be dealt with by the same methods. In the rock-salt lattice, we have two non-equivalent atoms in the positions:

	Na $(0, 0, 0)$;	Cl: $(\frac{1}{2}, 0, 0)$.
For zinc sulphide, Zn:	$(0, 0, 0)$	S: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.
For diamond,	C: $(0, 0, 0)$	C: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.
For fluorspar,	C: $(0, 0, 0)$	F: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$.

* For an explanation of this symbology reference should be made to the previous paper.

So far as the symmetry group is concerned, it is O_h for all cases except ZnS, and excepting the centre of inversion, all the other operations, forming the group T_d , can be located at a lattice point and this feature is common to all the four cases given above. Zinc sulphide has no centre of inversion, while for rock-salt it can be located at either Na or Cl atom, for diamond at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ and for fluorspar at (0, 0, 0). This shows that the normal modes of all the cases given above can differ only with respect to the centre of inversion. Each of the 8 possible vectors will now be taken up one by one and the normal modes evaluated by the methods fully explained in the earlier paper.

(1, 1, 1) *Vector*.—This is left invariant by all the operations of the point-group symmetry. Excepting the case for ZnS, which has T_d symmetry, the others have O_h symmetry and the reduced character of the operations is easily found when acting on the non-equivalent dynamical variables in each unit cell.

$$n_i = \frac{1}{N} \sum \psi(R) \chi^i(R)$$

	E	3 C ₂	8 C ₃	6 σ	6 S ₄	i	3 σ	8 S ₆	6 C ₂	6 C ₄	n_i (NaCl)	n_i (C)	n_i (ZnS)	n_i (CaF ₂)
A _{1g}	..	1	1	1	1	1	1	1	1	1
A _{2g}	..	1	1	-1	-1	1	1	1	-1	-1
E _g	..	2	2	-1	0	0	2	2	-1	0
F _{1g}	..	3	-1	0	-1	1	3	-1	0	-1	1	..	1	..
F _{2g}	..	3	-1	0	+1	-1	3	-1	0	+1	-1	1
A _{1u}	..	1	1	1	1	-1	-1	-1	-1	-1
A _{2u}	..	1	1	-1	-1	-1	-1	-1	+1	+1
E _u	..	2	2	-1	0	0	-2	-2	1	0	0
F _{1u}	..	3	-1	0	-1	1	-3	1	0	1	-1
F _{2u}	..	3	-1	0	1	-1	-3	1	0	-1	1	2	1	2
NaCl ψ	..	6	-2	0	2	-2	-6	2	0	-2	2			
Diamond ψ	..	6	-2	0	2	-2	0	0	0	0	0			
Zn S ψ	..	6	-2	0	2	-2			
CaF ₂ ψ	..	9	-3	0	3	-3	+1	0	-1	1				

The last four rows give the reduced character ψ of the operations when acting on dynamical variables of the four crystal lattices. The difference in the location of the inversion in NaCl and diamond is reflected by the fact

that in the former all the six modes are anti-symmetric with respect to inversion, while in the latter they separate out into symmetric and anti-symmetric modes. ZnS has no inversion and its six modes occur in F_{2u} . For CaF_2 , the mode F_{2g} gives one triply degenerate normal mode symmetric with respect to inversion while two other modes with degeneracies 3 each come under F_{2u} . If we exclude translations, these give, as is at once evident from the character table, the following frequencies:

	Degeneracy
(1) An oscillation of the sodium lattice against the chlorines in NaCl	3
(2) A mutual oscillation of the interpenetrating lattices in diamond	3
(3) A mutual oscillation of the zinc and sulphur lattices against one another in ZnS	3
(4) An oscillation of the Ca and F ions in CaF_2 which is symmetric with respect to inversion (F_{2g}). Since the inversion is located at the calcium atoms, they must be at rest in this mode	3
(5) A combined oscillation of all the calcium and fluorine atoms which is totally antisymmetric with respect to inversion (F_{2u}). The translations also occur in F_{2u} . Hence the only possibility left is that the fluorines go one way and the calciums go the other way	3

This rigorous analysis can be compared with the treatment given in an earlier paper.

$(-1, -1, -1)$ vector referred to rhombohedral axes.—The vectors $(-1, 1, 1)$; $(1, -1, 1)$; and $(1, 1, -1)$ referred to rhombohedral system are equivalent to $(-1, -1, -1)$ and so there is a minimum degeneracy of 4 for frequencies of this set. We consider the $(-1, -1, -1)$ vector only.

The symmetry operations keeping this invariant form the group D_{3d} in all cases except ZnS where it is simply C_{3v} without the inversion. The analysis is similar to the earlier treatment.

For ZnS , the appropriate character table consists of the first three columns and first three rows only. The distribution of frequencies in rock-salt and diamond is similar, with degeneracies 1, 2, 1, 2. The former two are symmetric with respect to inversion while the latter two are antisymmetric. Since ZnS has no centre of symmetry to distinguish the modes, we get a coupling between these two sets, which can be resolved only by forming the potential energy. For CaF_2 there are two frequencies with degeneracies

	E	$2 C_3$	3σ	i	$2 C_3 \times i$	$3 \sigma \times i$	n_i (NaCl)	n_i (C)	n_i (ZnS)	n_i (CaF ₂)
A_{1g} ..	1	1	1	1	1	1	1	1	2	1
A_{2g} ..	1	1	-1	1	1	-1
E_g ..	2	-1	0	2	-1	0	1	1	2	1
A_{1u} ..	1	1	1	-1	-1	-1	1	1	..	2
A_{2u} ..	1	1	-1	-1	-1	1
E_u ..	2	-1	0	-2	1	0	1	1	..	2
(NaCl) ψ ..	6	0	2	0	0	0				
(Diamond) ψ ..	6	0	2	0	0	0				
(ZnS) ψ ..	6	0	2				
(CaF ₂) ψ ..	9	0	3	-3	0	-1				

1 and 2 respectively which are symmetric with respect to the inversion. On the other hand, there are four frequencies with degeneracies 1, 2, 1, 2 and antisymmetric with respect to inversion. There is a coupling here between the two single frequencies, with a similar coupling for the double modes.

The symmetry characters of the modes are at once evident from the character table. Those under A_{1g} are totally symmetric with respect to (x, y, z) and for a state of vibration represented by the $(-1, -1, -1)$ vector, this can only be in a direction normal to the (111) planes. All the normal co-ordinates of an atom ' r ' involve the term $x_r + y_r + z_r$. For rock-salt, this is a vibration of the (111) planes. Being symmetric with respect to inversion, the sodiums are at rest, and alternate (111) planes of chlorine atoms move oppositely and normal to themselves. The same description holds good for the diamond lattices. For zincblende, alternate (111) planes contain zinc and sulphur atoms respectively, and the exact relative magnitude through which they move depends upon the forces between them. Hence they occur coupled together with two frequencies under A_{1g} . In fluorspar a similar motion of (111) planes occurs except that the calciums must be at rest in A_{1g} because of the symmetric nature with respect to inversion.

Coming to A_{1u} the modes of rock-salt are the same as the above case for A_{1g} except that it is the chlorine atoms which are at rest, with the sodium atoms moving. Diamond has a similar vibration which is now antisymmetric with respect to inversion. Alternate (111) planes now go two against two, thus $++--$, etc. For zinc sulphide, there is no distinction between A_{1u} and A_{1g} , while for fluorspar we have two coupled modes both antisymmetric with respect to inversion. This is natural, since a motion with

the two fluorines going the same way leaves a twofold option for the calcium atom. Either the calcium can move in the same way or opposite way with respect to fluorine. Thus $\begin{matrix} \text{F} & \text{Ca} & \text{F} \\ \rightarrow & \rightarrow & \rightarrow \end{matrix}$ or $\begin{matrix} \text{F} & \text{Ca} & \text{F} \\ \rightarrow & \leftarrow & \rightarrow \end{matrix}$ are possible and both are antisymmetric with respect to the inversion at the calcium atom.

The representations E_g and E_u are double. It is easily seen from the group characters that they involve co-ordinates like $x_r - y_r$, $y_r - z_r$ or $z_r - x_r$ of an atom. They involve motions of the (111) planes in two directions in their own planes and these two directions are equivalent. For rock-salt, the same motion as described earlier takes place with either the chlorines at rest or the sodiums at rest. Alternate (111) planes move tangentially and in opposite phases in this motion. For diamond also, a similar motion takes place, and it is either symmetric or antisymmetric with respect to inversion. In the former case the alternate planes move as $+$ $-$ $-$ $+$ and in the second case they move as $+$ $+$ $-$ $-$, etc. In zincblende alternate (111) planes of the same sort move in opposite phases tangentially. As there is no inversion to distinguish the modes further, we get a coupled mode or E_g . In fluorspar, E_g gives a doubly degenerate mode which is uncoupled with any other. It is symmetric with respect to inversion and so calciums must be at rest with the fluorines going in opposite ways. Here also alternate (111) planes of fluorines move tangentially. For CaF_2 we get in E_u two coupled modes with degeneracy two each. As explained for the case of A_{1u} , this is natural, as the calcium atoms can move in the same or opposite ways with respect to the fluorines. The direction of motion however is tangential here unlike A_{1u} . This completes a description of all the modes for similar motions occurring for $(1, \bar{1}, 1)$ $(1, 1, \bar{1})$ and $(\bar{1}, 1, 1)$ planes corresponding to the three other vectors. Thus we get an extra degeneracy of four for every frequency belonging to $(-1, -1, -1)$. The distribution for this branch can hence be represented as

(1) Rock-salt:	Distinct frequencies with degeneracies	4, 4, 8, 8
(2) Diamond	„ „	4, 4, 8, 8
(3) Zincblende	„ „	4, 4, 8, 8
(4) Fluorspar	„ „	4, 8, 4, 4, 8, 8

We now turn to the final vector $(1, -1, -1)$. A detailed description of the geometric modes for this vector can be given as above, but we content ourselves here by merely indicating the character table and the number of the appropriate normal modes with their degeneracies. This vector is left invariant by the elements

- (i) the identity;
- (ii) the three two-fold rotations about the x , y and z axes, $3C_2$;

(iii) a reflexion σ_1 in a plane passing through x axis and bisecting the other two;

(iv) the products of σ_1 with $3C_2$ *i.e.*, $3C_2 \sigma_1$.

This is the symmetry group D_{2d} for a crystal with no centre of inversion such as ZnS. The addition of a centre of inversion in rock-salt and fluorspar brings in eight operations more $D_{2d} \times i$ and the total group is of order 16. In diamond, however, the inversion does not commute with all the operations in D_{2d} , particularly the three twofold rotations P_1, P_2, P_3 about the three cubic axes. Its association with these elements brings in translation operations thus

$$i P_1 i^{-1} = P_1 \tau_x \text{ or } i P_1 i^{-1} P_1^{-1} = \tau_x, \quad (2)$$

Since $i^{-1} = i$ and $P_1^{-1} = P_1$ this can be written as

$$(iP_1)^2 = \tau_x; (iP_2)^2 = \tau_y; (iP_3)^2 = \tau_z. \quad (3)$$

Hence the space group keeping the vector $(+1, -1, -1)$ invariant in diamond lattice cannot be resolved as the product of a point group and a translation group. The simplified formula (17) in the paper on general theory is not directly applicable here and we have to derive the full character table for the space group. All these complications can be avoided, if, for a moment, we regard the two non-equivalent atoms in diamond as being different. Consequently there will be no centre of inversion here and the pattern is exactly the same as for ZnS. Afterwards, when the normal modes for ZnS are written down, we can, if we choose, bring in the inversion and easily see what modification it can bring in the normal modes.

	E	P_1	P_2, P_3	$\sigma_1, \sigma_1 P_1$	$P_2 \sigma_1, P_3 \sigma_1$	n_i
A_1 ..	1	1	1	1	1	..
A_2 ..	1	1	1	-1	-1	..
B_1 ..	1	1	-1	1	-1	2
B_2 ..	1	1	-1	-1	1	..
E ..	2	-2	0	0	0	2
ψ ..	6	-2	-2	2	-2	..

We thus have two single modes (coupled) and two double modes (coupled). If the inversion is now introduced, the coupling is removed with the modes separating out according as they are, or are not, symmetric with respect to inversion. We have here a process of building up the representations of a group from its subgroups. The full method is explained in the paper on general theory. Since the inversion brings in the translations,

we first choose the group $D_{2d} \times$ translations for diamond. According to Clifford's work each representation of this group we need here, is merely the direct product of the representations for D_{2d} and the representation (1, -1, -1) of the translation group.

$$\text{Here} \quad \chi(\tau_x) = -\chi(\tau_y) = -\chi(\tau_z) = 1 \quad (5)$$

$$\text{Hence} \quad \chi(P_1 \tau_x) = \chi(P_1); \chi(P_2 \tau_y) = -\chi(P_2); \chi(P_3 \tau_z) = -\chi(P_3) \quad (6)$$

for all representations associated with this vector. We now append the inversion and derive the group table for $D_{2d} \times \{E, i\}$. Taking the representation B_1 it is easily seen that it is sent into the representation A_1 by the inversion. This is because the inversion changes P_1, P_2, P_3 into $P_1 \tau_x, P_2 \tau_y$ and $P_3 \tau_z$ the characters for which, however, are equal to $\chi(P_1), -\chi(P_2)$ and $-\chi(P_3)$ from (6).

$$\text{Thus} \quad \chi(P_1) \rightarrow \chi(P_1) \quad \chi(P_2) \rightarrow -\chi(P_2) \quad \chi(P_3) \rightarrow -\chi(P_3)$$

as a result of the inversion. Thus A_1 and B_1 are equivalent under the inversion and they give rise to a double representation in the space group. The degeneracy of the mode under B_1 is thus increased and as a consequence the coupling is removed. The representation E however is left invariant by the inversion and so we do not get any new combination of representations. This gives rise to two representations in the space group, one which is symmetric, and the other antisymmetric with respect to inversion. Accordingly, the distribution of the six normal modes in diamond lattice for this vector is 2, 2, 2. From the symmetry characters of A_1, B_1 and E the normal modes can be derived. They will be found to be identical with the descriptions given earlier.

For fluorspar and rock-salt, the inversion is also located at a lattice point and so commutes with the point group D_{2d} . Hence there is no need to bring in a space group, and the appropriate character table is given by the direct product of D_{2d} and the inversion group with two representations $\chi(i) = \pm 1$. The further analysis is then exactly the same as above and there is no real need to put it down here again. The distribution of the modes is the same as given in the earlier paper.

The author is highly thankful to his professor, Sir C. V. Raman, for his kind interest in this work and his many valuable suggestions during the progress of this work.

Summary

In this paper, the character tables for groups associated with vectors defining normal modes are given for four cubic crystals based on a face-centred Bravais lattice, viz., rock-salt, diamond, zincblende and fluorite. The method of deriving normal modes from these tables, described in an earlier paper, is illustrated here.

THE FREQUENCY SPECTRUM OF THE DIAMOND LATTICE

BY E. V. CHELAM

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

THE many remarkable physical properties which diamond exhibits and the fact that the element carbon of which it is a crystalline form occupies a unique position in the field of chemistry invest this substance with an altogether exceptional interest for the experimental physicist. There is good reason why the mathematical physicist should also regard diamond with special interest. It is the typical valence crystal, and as it belongs to the cubic system and has a relatively simple structure, its physical behaviour should be readily amenable to theoretical explanation and computation. Indeed, the diamond lattice may fairly be regarded as a test case for any theory of the solid state.

Ramaswamy (1930) observed a sharp and intense line with a frequency shift of 1332 cm.^{-1} in the Raman spectrum of diamond and interpreted the same as the "rest-strahlen frequency" of diamond. He established the correctness of this interpretation by showing that the observed frequency agrees perfectly with that calculated from the Nernst-Lindemann specific heat formula and less perfectly with the Debye "limiting frequency" for diamond. Ramaswamy also discussed the reason for the appearance of the rest-strahlen frequency as a Raman-shift in diamond, as contrasted with its non-appearance in the alkali halides. Ramaswamy's claim that 1332 cm.^{-1} is the fundamental vibration frequency of the diamond lattice has been fully confirmed by the theoretical work of Nagendra Nath (1934), Venkatarayudu (1938) and of Bhagavantam and Venkatarayudu (1939). Their investigations have made it clear that an oscillation of the two interpenetrating lattices of carbon atoms with respect to each other would have this frequency and that it would be active in the Raman effect.

Other experimental facts have however awaited a satisfactory explanation. Amongst these should be specially mentioned the observation by Bhagavantam (1930) of several other feeble lines in the Raman spectrum

of diamond with frequency shifts both larger and smaller than 1332 cm.^{-1} , the strongest of them having a frequency shift of 1158 cm.^{-1} . The significance of this observation as well as of the infra-red absorption data for diamond recorded by Julius, Angstrom, Reinkober (1911) and Robertson and Fox (1930) was far from being clear. To throw some light on these matters, Dr. Nagendra Nath (1937-40) made an elaborate investigation of the frequency spectrum of the diamond on the basis of the Born theory. His results however remained unpublished.

The subject entered on a new phase as the result of the investigations by P. G. N. Nayar (1941, 1942) of the luminescence and associated absorption spectra of diamond at liquid air temperatures. Nayar worked with some of the diamonds in the extensive collection made by Sir C. V. Raman, and his results showed conclusively that the lattice spectrum of diamond contains a whole series of *discrete* frequencies stretching from 1332 cm.^{-1} downwards to quite low values. To explain these results of Nayar, Sir C. V. Raman (1941) put forward a new theory of the lattice vibrations in crystals, the basis of which was the postulate that these vibrations are *repetitive patterns in space*, the unit of the pattern having dimensions either identical with or an integral multiple of the dimensions of the lattice cell in the crystal. This idea has received a precise mathematical form and a dynamical justification in the introductory paper of the present symposium by Sir C. V. Raman. It is there shown that a super-cell whose dimensions are twice as great as those of a lattice cell is the space-unit of the repetition-pattern of the atomic vibrations properly so called, while vibrations whose repetitive units are of still larger dimensions fall in the category of elastic vibrations.

The various modes of atomic vibration possible in diamond on the basis of the Raman theory have already been derived and discussed in an earlier paper by the present author appearing in the symposium. It will now be shown how an expression for their frequencies may be derived on the basis of a scheme of force-constants similar to that employed by Nagendra Nath and others in their investigations.

2. The Geometry of the Lattice

To enable us to proceed we require a suitable notation for the atoms in the lattice and their displacements. The eight atoms in the unit cube have the following positions:

1	2	3	4	
$(0, 0, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, 0)$	
5	6	7	8	(1)
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{3}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	

Atoms 2, 3, 4 can be obtained by primitive translations from 1 and 6, 7, 8 likewise from 5. The rotational and reflexional symmetry of the lattice is represented by 48 operations of the octahedral group. There are actually only two non-equivalent atoms in the lattice, 1 and 5, and these may be regarded as representative of two lattice systems. Each atom of a system is surrounded tetrahedrally by four atoms of the opposite system. These are its nearest neighbours. The next nearest neighbours of an atom are twelve in number and they come from the same system. Four atoms of type 2, four of type 3, and four of type 4 are the next nearest neighbours of 1. As an illustration, we give here all the next nearest neighbours of atom 5. Let us introduce operations t_x, t_y, t_z for translations through $(a, 0, 0)$; $(0, a, 0)$; $(0, 0, a)$, a being the length of the edge of an 8-atom cell. By combining these operations we can form a set of operations $t_x, t_y, t_z, t_y t_z, t_z t_x, t_x t_y$ and $t_x t_y t_z$, eight in number. These carry the 8-atom cell in fact into the 8 cells of a supercell containing 64 atoms. \bar{t}_x will be a translation through an opposite direction, *i.e.*, through $(-a, 0, 0)$. The symbol $5(t_x)$ may be used to denote an atom obtainable from 5 by the translation t_x . Similar notation can be used to denote for 6, 7, 8, etc. With this notation, the twelve next nearest neighbours of the atom can be indicated below as

$$\begin{aligned} 6_1 &= 6(\bar{t}_y \bar{t}_z); 6_2 = 6; 6_3 = 6(\bar{t}_y); 6_4 = 6(\bar{t}_z) \\ 7_1 &= 7(t_z \bar{t}_x); 7_2 = 7(\bar{t}_x); 7_3 = 7; 7_4 = 7(\bar{t}_z) \\ 8_1 &= 8(\bar{t}_x \bar{t}_y); 8_2 = 8(\bar{t}_x); 8_3 = 8(\bar{t}_y); 8_4 = 8. \end{aligned} \quad (2)$$

The notation $6_1, 7_2, 8_3$, etc., is very convenient and has been borrowed from Dr. Nagendra Nath's unpublished work. We are now in a position to illustrate how the normal modes can be derived.

3. The Equations of Motion

It has been explained in another paper that in a normal mode, it is sufficient to know the displacements of one atom and the relative displacements of the other atoms. These displacements are known when the normal co-ordinate is known. Further, in a normal mode all the atoms move with the same frequency. It is therefore sufficient to consider the equation of motion of a single atom. The kinetic energy of atom 5 is $2T = m(\dot{x}_5^2 + \dot{y}_5^2 + \dot{z}_5^2)$, all co-ordinates being displacements from the equilibrium position and parallel to the cubic axes. Since the equations of motion involve the derivative of the potential energy function with respect to x_5, y_5 , or z_5 it is enough if we consider terms of the potential energy involving these only. The energy function chosen in this case represents the valence forces, forces of angular distortion and interaction between the next nearest neighbours. Accordingly,

potential energy terms involving atom 5 can be represented as

$$2V = K (d_{15}^2 + d_{25}^2 + d_{35}^2 + d_{45}^2) + K_\alpha (\theta_{23}^2 + \theta_{31}^2 + \theta_{12}^2 + \theta_{14}^2 + \theta_{24}^2 + \theta_{34}^2) \\ + K_\alpha \sum_{r=1}^{12} \phi_{r5}^2 + K'' \sum_{r=1}^{12} D_{r5}^2. \quad (3)$$

The summation in the last two terms runs over the next nearest neighbours of atom 5. d_{15} represents the variation in the distance 1-5 while D_{r5} is the variation in the distance between atom 5 and one of its nearest neighbours, the atom r . θ_{rs} denotes the variation in the angle subtended at 5 by the atom ' r ' and ' s '. ϕ_{r5} denotes the variation in angle subtended by the atom ' r ' and 5 at the appropriate atom. In terms of cartesian co-ordinates, these are given by

$$d_{rs} = (x_r - x_s) \xi_{rs} + (y_r - y_s) \eta_{rs} + (z_r - z_s) \zeta_{rs} \quad (4)$$

and the same type of expressions for D_{rs} . Here ξ_{rs} , η_{rs} , ζ_{rs} are the direction cosines of the lines joining the ' r 'th atom to the ' s 'th atom. If (a_r, b_r, c_r) and (a_s, b_s, c_s) are their positional co-ordinates, and l_{rs} the distance between them

$$\xi_{rs} = \frac{a_r - a_s}{l_{rs}}, \quad \eta_{rs} = \frac{b_r - b_s}{l_{rs}}, \quad \zeta_{rs} = \frac{c_r - c_s}{l_{rs}}. \quad (5)$$

We also have,

$$p \theta_{rs} = \sqrt{3} d_{rs} - \sqrt{2} (d_{rt} + d_{st}), \quad (6)$$

where p is the distance between nearest neighbours in equilibrium configuration and ' t ' denotes the suffix of the atom at which ' r ' and ' s ' subtend the valence angle. Similar expressions hold for ϕ_{rs} . These relations enable us to write down the Hamiltonian in terms of cartesian co-ordinates and form the equations of motion. Differentiating the potential energy function and equating the rate of change of momentum to it, we get the following equation of motion for x_5 .

$$-m \ddot{x}_5 = \lambda x_5 = P x_5 - Q (x_1 + x_2 + x_3 + x_4) + S (x_{6_1} + x_{6_2} + x_{6_3} + x_{6_4}) \\ - U (x_{7_1} + x_{7_2} + x_{7_3} + x_{7_4} + x_{8_1} + x_{8_2} + x_{8_3} + x_{8_4}) \\ - R (y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4) \\ - V (y_{6_1} - y_{6_2} - y_{6_3} + y_{6_4} + z_{6_1} - z_{6_2} + z_{6_3} - z_{6_4}) \\ + V (y_{7_1} - y_{7_2} - y_{7_3} + y_{7_4} + z_{8_1} - z_{8_2} + z_{8_3} - z_{8_4}) \\ - U (y_{8_1} - y_{8_2} - y_{8_3} + y_{8_4} + z_{7_1} - z_{7_2} + z_{7_3} - z_{7_4}) \quad (7)$$

where $\lambda = (2\pi\nu)^2 m$, m being the mass of the carbon atom and ν the frequency.

$$P = \frac{4}{3} (K + 7 K_\alpha + 3 K''), \quad Q = \frac{1}{3} (K + 8 K_\alpha), \quad R = \frac{1}{3} (K - 4 K_\alpha), \\ S = \frac{2 K_\alpha}{3}, \quad U = \frac{K_\alpha}{6} + \frac{K''}{2}, \quad V = -\frac{K_\alpha}{3}. \quad (8)$$

4. The Expressions for the Frequencies

Once the equation of motion for x_5 is written out, we can substitute in it the known relative displacements of the other atoms in any chosen normal mode. The normal mode completely specifies the displacements of every atom in the cell in terms of x_5 and putting the values in (7) we get an expression for ν , the frequency. Among the normal modes we need pick out for consideration only eight, with only one each from a set of mutually equivalent degenerate modes. There are only eight such distinct frequencies and taking the cases one by one the expressions will be calculated. A knowledge of the normal co-ordinates is assumed here and can be easily taken over from earlier papers.

(1, 1, 1) vector. $\chi(t_x) = \chi(t_y) = \chi(t_z) = 1$;

$$x_5 = x_6 = x_7 = x_8 = x_{5_1} = x_{5_2} = \text{etc.}, = x_{8_1} = x_{8_2} = \text{etc.}, \\ = -x_1 = -x_2 = -x_3 = -x_4 = \text{etc.}$$

as all the eight super-cells go the same way, with the lattice systems 1 and 5 going the opposite ways. The y and z displacements are zero; substituting these we get

$$\lambda_1 = \frac{8K + 64K_\alpha}{3m}.$$

Degeneracy 3.

(-1, -1, -1) vector.

$$\chi(t_x) = \chi(t_y) = \chi(t_z) = -1.$$

Therefore $-u_5 = u_6 = u_8 = -u_{6_2} = -u_{6_4} = u_7 = u_8$, etc.,

and correspondingly for u_1, u_2 , etc. $u = x, y$, or z .

These relations hold for all frequencies of this vector.

λ_2 corresponds to the motion of alternate (1, 1, 1) planes normal to themselves.

Here $x_1 = y_1 = z_1 = -x_5 = -y_5 = -z_5$

with the relative displacements of the other atoms defined as above. Substituting

$$\lambda_2 = \frac{2K + 8K''}{m};$$

Degeneracy 4

λ_3 is defined by $x_1 = y_1 = z_1 = x_5 = y_5 = z_5$:

Degeneracy 6

$$\lambda_3 = \frac{2}{3m} (K + 32K_\alpha + 12K'')$$

λ_4 is defined by $z_1 = -x_1 = -z_5 = x_5$:

Degeneracy 8

$$\lambda_4 = \frac{8K + 34K_\alpha}{3m} + \frac{2K''}{m}$$

λ_5 is defined by $z_1 = -x_1 = z_5 = -x_5$:

Degeneracy 8

$$\lambda_5 = \frac{6K_\alpha + 2K''}{m}.$$

In these modes the relative displacements of all the atoms equivalent to 1 or 5 must be derived from the characteristic relations defined by the vector (1, 1, 1). On substituting all these, the expressions given above are obtained. (1, -1, -1) vector

λ_6 defined by $x_5 = x_6 = -x_7 = -x_8$

$$\lambda_6 = \frac{4K + 40K_a}{3m} + \frac{8K''}{m} : \quad \text{Degeneracy 6.}$$

The motion of the rest of the atoms is defined by the above vector.

For λ_7 and λ_8 involving motions in tangential directions there is no displacements of the x co-ordinate so far as this vector is concerned. Since we have written down the equation for x_5 , it is convenient to consider the (-1, 1, -1) or (-1, -1, 1) vectors for λ_7 and λ_8 .

$$z_1 = -z_2 = z_3 = -z_4 = x_5 = -x_6 = x_7 = -x_8$$

$$\text{and } z_1 = -z_2 = z_3 = -z_4 = -x_5 = x_6 = -x_7 = x_8$$

define the two modes for (-1, 1, -1) vector. Substituting these relations, we get

$$\lambda_7 = \frac{12K_a + 4K''}{m} : \quad \text{Degeneracy 6}$$

$$\lambda_8 = \frac{8K + 4K_a}{3m} + \frac{4K''}{m} : \quad \text{Degeneracy 6}$$

This completes all the 8 frequencies. We finally present in a tabular form all the 8 frequencies with their degeneracies.

Frequency Number	Description	Magnitude	Degeneracy
λ_1	Two lattices moving oppositely	$\frac{8K + 64K_a}{3m}$	3
λ_2	Motion of alternate sets of octahedral planes as fully explained in earlier papers	$\frac{2K + 8K''}{m}$	4
λ_3		$\frac{2}{3m} (K + 32K_a + 12K'')$	4
λ_4		$\frac{8K + 34K_a}{3m} + \frac{2K''}{m}$	8
λ_5		$\frac{6K_a + 2K''}{m}$	8
λ_6		$\frac{4K + 40K_a}{3m} + \frac{8K''}{m}$	6
λ_7	Motion of alternate cubic planes as explained in earlier papers	$\frac{12K_a + 4K''}{m}$	6
λ_8		$\frac{8K + 4K_a}{3m} + \frac{4K''}{m}$	6

The author has the greatest pleasure in acknowledging his indebtedness to Sir C. V. Raman, Kt., F.R.S., N.L., for his kind suggestions and constant encouragement during the course of this work. The author is also extremely obliged to his professor, Dr. N. S. Nagendra Nath, M.Sc., Ph.D., under whose direction and guidance a very considerable part of this work was conducted. The notation has also been borrowed from his unpublished work. He also wishes to express his thanks to Prof. S. Bhagavantam for his kind interest in this work.

Summary

The eight frequencies in a diamond lattice are calculated with a suitable force field and explicit expressions are given for them. Sir C. V. Raman's theory of superlattice vibrations is the basis of the investigation.

REFERENCES

- | | |
|--|--|
| S. Ramaswamy | .. <i>Ind. Jour. Phys.</i> , 1930, 5 , 97. |
| N. S. Nagendra Nath | .. <i>Proc. Ind. Acad. Sci. A</i> , 1934, 1 , 333. |
| T. Venkatarayudu | .. <i>Ibid.</i> , 1938, 8 , 349. |
| S. Bhagavantam and
T. Venkatarayudu | .. <i>Ibid.</i> , 1939, 9 , 224. |
| S. Bhagavantam | .. <i>Ind. Jour. Phys.</i> , 1930, 5 , 573. |
| Reinkober | .. <i>Ann. Der. Phys.</i> , 1911, 34 , 343. |
| Robertson and Fox | .. <i>Phil. Trans. Roy. Soc.</i> , 1934, 232 , 463. |
| P. G. N. Nayar | .. <i>Proc. Ind. Acad. Sci. A</i> , 1942, 15 , 293. |
| Sir C. V. Raman | .. <i>Ibid.</i> , 1941, 14 , 459. |
| | .. <i>Ibid.</i> , 1943, 18 , 237. |

MODES OF VIBRATION OF THE HEXAGONAL CLOSE-PACKED LATTICE

BY G. N. RAMACHANDRAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 10, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

THE hexagonal close-packed structure is a frequently encountered atomic arrangement in the crystalline form of many metallic elements. It is associated with a hexagonal unit cell having the axial ratio c/a equal to 1.63, and is a closest packing of spheres. The unit cell contains two atoms which have the co-ordinates 0, 0, 0; $2/3, 1/3, 1/2$. In some metals, the axial ratio is slightly different from 1.63, but the co-ordinates of the atoms is the same. In this paper, the modes of vibration of the hexagonal close-packed structure are investigated on the basis of the fundamental ideas proposed by Sir C. V. Raman in an earlier paper. The results are true for any hexagonal structure in which there are atoms at 0, 0, 0; $2/3, 1/3, 1/2$ and is not restricted to the case where the axial ratio is 1.63.

In a preceding paper, the author has discussed the modes of vibration of a simple hexagonal Bravais lattice, and has shown that the eight types of vibration fall into four sets, namely $(+++)$; $(++-)$; $(+-+)$, $(-++)$, $(--+)$; $(+- -)$, $(-+-)$, $(---)$. We shall now take up each of these sets, and discuss the modes of the close-packed lattice under it, using group theoretical methods. In this connection, it must be noted that the crystal belongs to the space-group $D_{6h}^{4/2}$, in which the inversion is not at a lattice point, but is at a point midway between the two atoms, i.e., at $1/3, 1/6, 1/4$. Hence, the method used by E. V. Chelam in an earlier paper in discussing the vibration of the diamond lattice is employed for deriving the character table and the modes of vibration.

2. The $(+++)$ and $(++-)$ Types of Vibration

We first consider the two atoms in the unit cell to be different, so that there is no centre of inversion. Then, the group of the vibration (cf. earlier paper by the author) is D_{3h} , whose character table is drawn up below. The reduced character $\psi(R)$ for each of the operations in the $+++$ type is tabulated below against ψ_{+++} . Thus, two vibrations (coupled) are

obtained under A_2'' and two others coupled under E' . On introducing the centre of inversion, the coupling is removed, the modes splitting up into two, symmetric and antisymmetric with respect to inversion. Also, it is easily seen that these modes are distinct. They represent the three translations of the lattice as a whole, and three vibrations of the two interpenetrating lattices against one another, one being along the hexagonal axis and the other two degenerate in the perpendicular plane.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2$	$3\sigma_v$	n_i (+ + +)	n_i (+ + -)
A_1'	1	1	1	1	1	1	..	1
A_2'	1	1	1	1	-1	-1
A_1''	1	-1	1	-1	1	-1
A_2''	1	-1	1	-1	-1	1	2	1
E'	2	2	-1	-1	0	0	2	1
E''	2	-2	-1	1	0	0	..	1
ψ_{+++}	6	2	0	-4	-2	2		
ψ_{++-}	6	0	0	0	0	2		

Coming to the $++-$ type of vibration, it has been shown by the author (*loc. cit.*) that for the simple hexagonal lattice, the group of the vibration is D_{6h} . In the present case, if we consider the two atoms to be distinct, there is no centre of inversion, and the group is only D_{3h} , which is the same as for $+++$. The reduced character for this is tabulated in the character table against ψ_{++-} and the number of modes n_i under each state is determined. It is found that there is one mode each under A_1' , A_2'' , E' and E'' . On introducing the centre of symmetry, and associating it with the operations of the group D_{3h} , the translation operators are brought in thus:

$$i\sigma_h i^{-1} = \sigma_h \tau_z; iC_3 i^{-1} = C_3 \tau_x; iS_3 i^{-1} = S_3 \tau_x \tau_z; iC_2 i^{-1} = C_2 \tau_x \tau_z; i\sigma_v i^{-1} = \sigma_v \tau_x.$$

Hence, the operations of D_{3h} do not commute with the inversion, and the group $D_{3h} \times i$ contains the product of the operations of D_{3h} and the translations. It has been shown by Chelam (*loc. cit.*) that the character of the product of an operation R of the point-group and a translation T is the product of their characters, i.e., $\chi(RT) = \chi(R) \chi(T)$. Thus, on introducing the inversion, the following transformations occur:

$\chi(\sigma_h) \rightarrow -\chi(\sigma_h)$; $\chi(C_3) \rightarrow \chi(C_3)$; $\chi(S_3) \rightarrow -\chi(S_3)$; $\chi(C_2) \rightarrow -\chi(C_2)$ and $\chi(\sigma_v) \rightarrow \chi(\sigma_v)$. Hence, the representations A_1' and A_2'' are sent one into the other and so are E' and E'' . Thus these are equivalent under the inversion and give rise respectively to a double and a quadruple representation in the space-group. Thus, the vibrations symmetric and antisymmetric

with respect to the inversion are identical. Hence, under this type, we have a vibration along the hexagonal axis with degeneracy 2, and another degenerate in the perpendicular plane with degeneracy 4.

3. The Remaining Types of Vibration

The vibration represented by the set $(+ - +, - + +, - - +)$ denotes the vibration of atoms in alternate prismatic planes. Taking one of them, $+ - +$, it is easily seen that the group of the vibration is only C_{2v} , if the two atoms are considered distinct. The character table is given below. The transformations on introducing the inversion are $iC_2i^{-1} = C_2\tau_x\tau_z$; $i\sigma_v i^{-1} = \sigma_v\tau_x$; $i\sigma_v' i^{-1} = \sigma_v'\tau_z$. These keep the representations invariant, so that each of them splits into two, one symmetric and the other anti-symmetric, with respect to the inversion. In these, the successive atomic planes have the phases $+ - - +$ and $+ + - -$ respectively. These are distinct since the planes are not equally spaced.

C_{2v}	E	C_2	σ_v	σ_v'	n_i (+ - +)	n_i (+ - -)
A_1	1	1	1	1	2	2
B_2	1	-1	-1	1	2	1
A_2	1	1	-1	-1	2	1
B_1	1	-1	1	-1	2	2
$\psi + - +$	6	-2	2	2		
$\psi + - -$	6	0	2	0		

The last set $(+ - - , - + - , - - -)$ represents vibrations of atoms in diagonal planes of the type $(01\bar{1}1)$. For this also, the group of the vibration is C_{2v} and taking one of the types, $+ - -$, the values of ψ and n_i are shown in the above character table. Using the transformations in the previous paragraph, it is seen that the representations A_2 and B_2 become equivalent, and so do A_1 and B_1 . Thus, we get a doubly degenerate vibration antisymmetric to σ_v , and two coupled doubly degenerate vibrations symmetric to it. The direction of the former is parallel to the plane and perpendicular to the hexagonal axis. It may also be described as the intersection of the vibrating plane with the horizontal reflection plane of the lattice. The other two vibrations take place in two unspecifiable directions in the perpendicular plane σ_v . A physical explanation for the equivalence of the symmetrical and antisymmetrical modes consists in the fact that the vibrating planes may be imagined to be either the $(01\bar{1}1)$ or the $(01\bar{1}\bar{1})$ planes.

The modes of vibration may thus be described as follows:—

No.	α	β	γ	Description	Number of modes
1, 2	+	+	+	Translation of the lattice as a whole	1, 2
3	+	+	+	Vibration of the atoms in the two lattices against each other, in a direction parallel to the hexagonal axis Oz	1
4	+	+	+	Same as (3), but in a plane perpendicular to Oz, the vibration being degenerate in the plane	2
5	+	+	-	Vibration of basal (0001) planes with the phases (+ + - -) and (+ - - +) normally	2
6	+	+	-	Same as (5), but transversely degenerate in the plane ..	4
7 to 9	+	-	+	Vibrations of prismatic planes in three directions, normally, transversely perpendicular to the hexagonal axis, and parallel to it, with the phases + + - -	3, 3, 3
10 to 12	do	-	-	Same as (7) to (9) but with the phases + - - + ..	3, 3, 3
13	+	-	-	Vibration of the (01 $\bar{1}$ 1), (10 $\bar{1}$ 1), (1 $\bar{1}$ 01) planes with the phases (+ + - -) and (+ - - +) in a direction in the plane perpendicular to the hexagonal axis	6
14, 15	do	-	-	Same as (13), but in two unspecified directions in a plane perpendicular to the direction in (13), as described above	6, 6
Total ..					48
Number of distinct modes ..					13

In conclusion, I wish to express my grateful thanks to Prof. Sir C. V. Raman for the keen interest that he took in the investigation.

Summary

The modes of vibration of the hexagonal close-packed structure is worked out on the basis of the Raman theory of crystal vibrations. The character tables are drawn up, and the vibrations are derived by a method due to E. V. Chelam without using the character table of the space-group. It is found that there are 13 vibrations with degeneracies 1, 2, 2, 4, 3, 3, 3, 3, 3, 6, 6, 6. The planes which take part in each mode and the directions of vibration for these are also described.

ON MARIS AND HULBURT'S ULTRAVIOLET LIGHT THEORY OF AURORÆ AND MAGNETIC STORMS

BY TA-YOU WU

(*Department of Physics, National University of Peking, and Institute of Astronomy, Academia Sinica, Kun-ming, China*)

Received October 26, 1943

(Communicated by Sir C. V. Raman, kt., F.R.S., N.L.)

IN a series of papers, Maris and Hulburt have developed an ultraviolet light theory of auroræ and magnetic storms.¹ The theory is not subject to the difficulty pointed out by Schuster and by Lindemann against the corpuscular theory, and is claimed to give a satisfactory explanation of the concentration of the auroræ in the region of high latitudes, the diurnal variations of magnetic storms, etc. The theory is based on the following assumptions: (1) The $\sim 10^{16}$ atoms or molecules (called simply particles here) in a column of unit cross-section above ~ 450 km. bounce up and down with exceedingly long free paths and make $\sim 10^{14}$ collisions per second at the 450 km. level. The particles at this level are excited to high energy states or ionized by solar radiations. In collisions of the second kind with these excited particles or in collisions with recombining particles, the particles from above receive energies corresponding to velocities as high as 10 km./sec. It is assumed that some 10^8 of these 10^{14} collisions are of this nature. The particles will reach some 40,000–80,000 km. in 3 to 6 hours. (2) These high flying particles are ionized by solar radiations in 3 to 6 hours and, being now electrically charged, come down in spirals around the lines of force of the earth's magnetic field. These ions coming down into the lower atmosphere produce the auroræ, etc.

This theory has been examined by Chapman and its consequences have been compared with the observed facts.² Mitra and Banerjee have made some calculations on the basis of this theory and obtained somewhat different values for the number of particles sent up per second and the time

¹ H. B. Maris and E. O. Hulburt, *Phys. Rev.*, 1929, 33, 412; Hulburt, *ibid.*, 1929, 34, 344; 1930, 36, 1560; *Rev. Mod. Phys.*, 1937, 9, 44.

² S. Chapman, *Monthly Notices, Roy. Astro. Soc. Geophys. Supp.*, 1930, 2, 296; *Terr. Mag.*, 1938, 43, 77. These papers are not available to the writer who comes across reference to the first in the articles by Hewson, *Rev. Mod. Phys.*, 1937, 9, 430, and Hulburt, *Phys. Rev.*, 1930, 36, 1560, to the second in *Science Abstracts*, No. 2814, 1938.

taken for the ionization of these particles.³ The purpose of this note is to examine more closely the fundamental processes assumed by Maris and Hulburt and the calculations of Mitra and Banerjee.

Granting that the distribution of particle density with height is what the original authors assume, we can show that the number of particles receiving a high velocity by the assumed mechanism is extremely small. Consider first the possibility of a particle acquiring a high velocity by a collision of the second kind with an excited atom or molecule at the 450 km. level. The ratio of the concentrations of particles in an excited state k and in the ground state i may be expected to differ greatly from the Boltzmann factor on account of the low pressure and hence the scarcity of collisions in the upper atmosphere. To obtain the relative populations it would be necessary to treat the problem as one of radiative equilibrium in diluted temperature radiation according to the theory of cycles of Rosseland. For the consideration of the order of magnitude only, we may simplify the problem by considering only the state i , the state k and the continuum c so that we have

$$N_i B_{\uparrow i}^k \rho(\nu) + N' \int_0^\infty \nu Q(\nu) N_e(\nu) d\nu = N_k A_{\downarrow i}^k + N_k \int_{\nu_0}^\infty \frac{\tau(\nu)}{h\nu} I(\nu) d\nu, \quad (1)$$

where N_i , N_k , N' , $N_e(\nu) d\nu$ are the concentrations of particles in the states i , k and the ionized state, and of electrons having velocities between ν and $\nu + d\nu$, respectively, $Q(\nu)$ is the cross-section for electron capture by the ion into the state k , $\tau(\nu)$ the cross-section for photo-ionization of the state k , $I(\nu)$ the intensity of solar radiation of frequency ν , and $B_{\uparrow i}^k$ and $A_{\downarrow i}^k$ are the Einstein coefficients of absorption and spontaneous emission respectively. It can readily be verified that the second term of the right-hand side of (1) is very small compared with the first, and for electron capture cross-section of the order 10^{-21} cm.² and total electron density less than 10^6 /c.c., the second term on the left of (1) is small compared with the first so that approximately

$$N_k/N_i = (g_k/g_i) B_{\uparrow i}^k / A_{\downarrow i}^k = \frac{g_k}{g_i} \frac{c^3}{8\pi h \nu^3} \rho(\nu), \quad (2)$$

where $\rho(\nu)$ is the radiation energy density at frequency ν , $h\nu = E_k - E_i$ and the g 's are the statistical weights. ρ can be taken to be W times that of a black body at $T = 6000^\circ$ K. where W is the dilution factor and is $\sim 5 \times 10^{-6}$. For $E_k - E_i = 13$ volts so that one half of it when transferred to a colliding particle of the mass of an oxygen atom may give it a velocity ~ 9 km./sec.,

³ S. K. Mitra and A. K. Banerjee, *Indian J. Phys.*, 1939, 13, 107.

the above ratio N_k/N_i is $\sim 10^{-16} g_k/g_i$. Thus of the 10^{14} collisions between the particles from above and those below, only $\sim 1/10^2$ of a collision takes place with an excited atom or molecule. Furthermore, the probability of energy transfer from an excited atom or molecule to a heavy particle is known to be very small, probably of the order of $10^{-3} - 10^{-1}$ per collision, when the energy must go into the kinetic energy of translation of the heavy particle. This small probability is due to the great disparity in the masses of the electron and the heavy particle. Hence of the 10^{14} collisions, only $10^{-5} - 10^{-3}$ of a collision, not 10^8 as Maris and Hulburt assumed, will result in imparting a high velocity to the particle from above.

Consider next the plausibility of a particle from above acquiring a high velocity on collision with recombining particles below. Now this is a three-body process and as such the probability is extremely small on account of the low pressure in the upper atmosphere. This probability can be expressed in terms of a cross-section of the recombination for unit concentration of the third body. On making an optimum assumption that the probability of the energy transfer in a given collision is $\sim 1/100$, this cross-section for unit concentration of the third body is $\sim 10^{-42} \text{ cm}^5$.⁴ At a height where the concentrations of the recombining particles and of the third body are all of the order $10^{10}/\text{c.c.}$, the number of 3-body collisions is about 10^{-7} per second per c.c. Thus the number of particles acquiring a high velocity from recombining particles is too small to play any role in producing auroræ.

Consider now the calculations of Mitra and Banerjee for the number of particles sent up in collisions of the second kind between an atom and an oxygen atom in the metastable state 1S formed by the capture of an electron by an oxygen ion O^+ produced by photo-ionization. The probability of ionization is given, as in (1), by

$$w = \int_{\nu_0}^{\infty} \frac{\tau(\nu)}{h\nu} I(\nu) d\nu \quad (3)$$

where the atomic absorption coefficient $\tau(\nu)$ is $\sim 1.4 \times 10^{-17}$ according to Bates, Buckingham, Massey and Unwin.⁵ One has then $w \sim 1 \times 10^{-8}$ so that of the 10^{16} particles in a column of unit cross-section above $\sim 770 \text{ km.}$, about 1×10^{-8} are ionized per second. The number of recombinations forming $O(^1S)$ in the column per second is given by $q = \alpha N_+ N_- L$ where α is the recombination coefficient for radiative process, N_+ , N_- are the

⁴ Cf. H. S. W. Massey, *Negative Ions*, Cambridge Univ. Press, 1938.

⁵ Bates, Buckingham, Massey and Unwin, *Proc. Roy. Soc.*, 1939, A 170, 322.

concentrations of O^+ and electrons and L is the height of the column such that $N_+ L =$ total number of O^+ in the column. Now Mitra and Banerjee obtained a value 10^5 for q by putting $q = \alpha n_+ n_-$ where n_+ , n_- are the numbers of O^+ and electrons produced in the column per second, a procedure which is obviously incorrect. To obtain an estimate of q , we need, not the numbers of O^+ and electrons produced per second in the column, but the concentrations and the total numbers present at a certain moment. The total number of O^+ in the column after irradiation by solar radiations for some 10^4 seconds (a few hours) is of the order 10^{12} . This number of O^+ and hence also of electrons must be spread over a great height so that the electron density N_- is probably of the order $10^3/\text{c.c.}$ (it cannot be much greater, for otherwise it would have been revealed by observations on the reflection of radio waves). As α is of the order 10^{-13} according to Bates *et al.*,⁵ one finds for q a value $\sim 10^2$ per second. As the lifetime of the state 1S of OI is 0.5 second and as the collision frequency at the level 800–900 km. is about one in 75 seconds, these 10^2 $O(^1S)$ atoms make about 1 collision per second with other atoms. Of this only a fraction, say γ , will be of the second kind, where γ is the efficiency of energy transfer and is certainly less than unity. It is then clear that the process considered by Mitra and Banerjee is inadequate in accounting for the auroræ and magnetic storms. Incidentally it may be pointed out that the 4.2 volts of energy released in the process $^1S \rightarrow ^3P$ in the oxygen atom will be divided between the two colliding atoms on momentum considerations so that the energy available for shooting the atom is only about 2 volts.

The above considerations also make it clear that no material changes in order of magnitudes of the various quantities will be obtained for the case of an active sun.

Finally, the assumption that the high flying atoms are ionized by solar radiations in 3 to 6 hours is based on the relation

$$E = t(I_0 - I) = tI_0(1 - e^{-\tau}), \quad (4)$$

where E is the ionization potential of the particle, t is the time in which the particle is ionized, I_0 and I are the intensities of the ionizing radiations before and after traversing a column of unit cross-section and of such height that it contains just one particle, and τ is the atomic absorption coefficient defined by the usual relation $I = I_0 e^{-N\tau x}$. Mitra and Banerjee employed the relation (4) and found $t = 3 \times 10^3$ hours. Now the above relation for t implies that the atom continues to absorb energy from the radiation beam for a time t until it amounts to the ionization potential E . This is entirely at variance with the basic idea in the quantum theory in which the

process is governed entirely by probability considerations. The time t should be given by the relation

$$t = 1/w, \quad (5)$$

where w is the number of transitions per second from the bound state to the continuous state under the action of the radiation field. As ionization can be effected by all radiations with frequency ν greater than the value ν_0 corresponding to E , the total probability of ionization by solar radiations is simply that given by (3) and is of the order 10^{-8} per second. Hence the lifetime of the neutral oxygen atom is $\sim 10^8$ seconds instead of the values assumed by Maris and Hulburt and calculated by Mitra and Banerjee on the basis of (4).

Thus on the above general considerations, it is clear that the assumed physical picture of the processes invoked in the theory of Maris and Hulburt is inadequate for explaining the cause of auroræ and magnetic storms.

ELECTROLYTIC SOLUTION PRESSURE OF COPPER WIRES UNDER STRAIN

BY LAJJA RAM GAUTAM AND J. B. JHA

(The Chemical Laboratories, Agra College, Agra)

Received January 25, 1943

(Communicated by Prof. N. K. Sethi, D.Sc., F.A.Sc.)

It is long since known that the tension existing on the surface of the metals has a considerable influence on the potentials of the metals in solution of its salts and therefore it has been found necessary to fix definite conditions for the preparation of the electrodes.

Uptil now no systematic study has been undertaken to establish a relationship between these strains and the electrolytic solution pressures. This is clearly due to the fact that strains are difficult to measure. The solitary instance of an attempt to study the effect is by M. G. Moore¹ who had done experiments to determine any change in the energy of emergence with change in the state of strain of the metal surface. The difference between the energy of emergence of the strained and unstrained surfaces was measured by the difference in the contact potential. His experiments showed that with an expansion of 1% the change in the energy of emergence was certainly less than 4×10^{-3} volts. His experiments were not intended to investigate any relation between strain and electrolytic solution pressure and therefore are of little use.

The experiments mentioned herein are an attempt for a systematic study of P. D. between strained and unstrained metallic surfaces dipping in solution of a metallic salt. As a result it is found that molecular aggregation on the surface of the strained wires plays an important part in the values of potential differences.

For the purpose of these experiments two copper wires were annealed by heating them till red hot and then dipping in methyl alcohol. This treatment has been found to give reversible copper electrodes. An electrolytic cell was prepared as shown in Fig. 1, one of the wires marked A was loose and without any strain while the other wire B was strained by suspending weights.

The cell C was filled with copper sulphate solutions of definite and known strength. An E.M.F. was found to develop between the strained and unstrained wires. The galvanometer used was a suspended coil mirror type made by Cambridge Instrument Co., Ltd., England, and had a sensitivity giving 1 m.m. deflection for a current of 4×10^{-9} amp. The

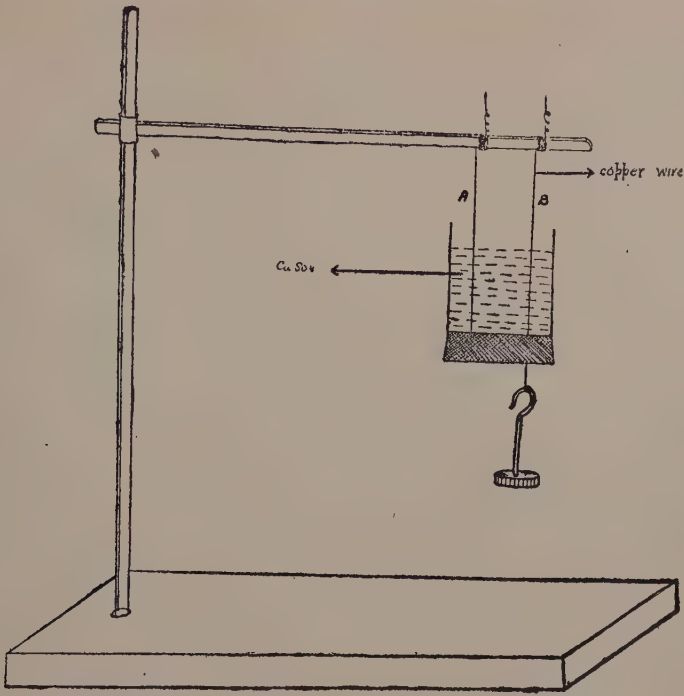


FIG. 1

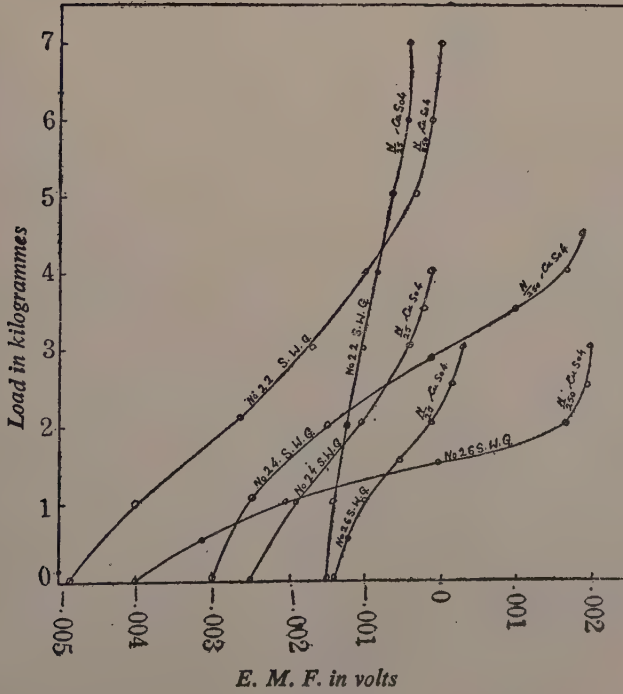


FIG. 2

resistance of the galvanometer was 450 ohms. The arrangement permitted the fall of potential of $\cdot 00001$ volt being easily detected. The measurements were made by a potentiometric arrangement. The results of the experiments have been shown in the tables and graphs attached.

TABLE I

*The Copper Wire No. 22 S.W.G.
in N/25 Copper Sulphate Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0015$ volt
1	$-\cdot 0014$
2	$-\cdot 0012$
3	$-\cdot 0010$
4	$-\cdot 0008$
5	$-\cdot 0006$
6	$-\cdot 0004$
7	$-\cdot 0004$

TABLE II

*The Copper Wire No. 24 S.W.G.
in N/25 CuSO_4 Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0025$ volt
1	$-\cdot 0019$
2	$-\cdot 0010$
3	$-\cdot 0004$
3.5	$-\cdot 0002$
4	$-\cdot 0001$

TABLE III

*The Copper Wire No. 26 S.W.G.
in N/25 CuSO_4 Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0014$ volt
0.5	$-\cdot 0012$
1	$-\cdot 0010$
1.5	$-\cdot 0005$
2	$-\cdot 0001$
2.5	$+\cdot 0002$
3	$+\cdot 0003$

TABLE IV

*The Copper Wire No. 22 S.W.G.
in N/250 CuSO_4 Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0049$ volt
1	$-\cdot 0040$
2	$-\cdot 0025$
3	$-\cdot 0017$
4	$-\cdot 0010$
5	$-\cdot 0003$
6	$-\cdot 0001$
7	$\cdot 0000$

TABLE V

*The Copper Wire No. 24 S.W.G.
in N/250 CuSO_4 Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 003$ volt
1	$-\cdot 0025$
2	$-\cdot 0015$
3	$-\cdot 0002$
3.5	$+\cdot 0010$
4	$+\cdot 0017$
4.5	$+\cdot 0019$

TABLE VI

*The Copper Wire No. 26 S.W.G.
in N/250 CuSO_4 Solution*

Load applied (Kilogrammes)	E.M.F. Observed
0	$-\cdot 0040$ volt
0.5	$-\cdot 0031$
1	$-\cdot 0020$
1.5	$\cdot 0000$
2	$+\cdot 0017$
2.5	$+\cdot 0020$
2.75	$+\cdot 0020$

The constant term E_0 in the Nernst expression $E = E_0 + \frac{RT}{nF} \log c$ has been evaluated by Butler.² He puts the constant term E_0 as being equal to $\frac{W_1 - W_2}{nF} + \frac{RT}{nF} \log \frac{A N_s}{1000 N_1 A_1}$ where W_1 is the work required to bring a positive ion from the metallic surface to the equilibrium point, similarly W_2 represents the work required to bring a negative ion from the bulk of the solution to the equilibrium point, $A_1 = V \sqrt{R/n W_1}$, $A = \sqrt{R/2 \pi M}$, M being the gram ion weight, N_1 = number of ions per unit area of the metal surface, N_s = number of ions per c.c. of the salt solution. Other symbols having their usual meanings. Of the two terms occurring in the equation, the first term $\frac{W_1 - W_2}{nF}$ is the only significant one and has a predominant value, the other terms according to Butler (*loc. cit.*) can be left out.

W_1 is the work done in bringing the metallic ion from the surface of the metal to the equilibrium point. Butler (*loc. cit.*) has not taken account of any resistance that would have to be overcome in detaching the metallic ion from the molecular aggregation.

The aggregates of crystals in the metals are of great complexity. When the metals are strained for instance as happens when they are stretched by a load, these aggregates which sometimes are as big as a fraction of a millimetre are altered. Ewing and Rosenhain³ have made a special study of this fact and find that when a metal is strained beyond the yield point there is a slipping of the crystals as shown in Figs. 3 and 4.

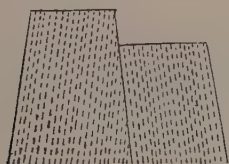


FIG. 3
Before Straining

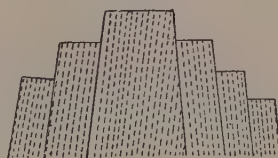


FIG. 4
After Straining

The increase in the positive value of P.D. of the strained wire shows that the tendency for the copper to form ions under stretching strain becomes less as the weight is increased (Fig. 2) or that the molecular aggregates formed on the surface hinder the formation of ions. This means that the value of W_1 in the case of strained wire is higher than in the case of annealed one.

It is also seen that when the strain is removed the P.D. against the annealed wire does not reach its original value showing that the

molecular aggregates and not the strain itself is responsible for the increase in the potential.

It is very difficult to keep wires free from any strain and therefore the curves have started from different E.M.F.'s although dipping in the same solution shown in Fig. 2.

It is also seen from the graph (Fig. 2) that after a certain load the P.D. becomes constant. This may be due to the fact that at this stage the wire approaches the breaking point and the deformation at the electrode surface is complete.

Conclusion

1. The potential differences of copper wires under stretching strain against annealed wires have been studied.

2. It is found that the strained wire is more positive.

3. It is contended that some work is necessary to detach ions from the metallic surface and is more in the case of strained wire as compared to the annealed one.

REFERENCES

- | | |
|------------------------|---|
| 1. Erlanger | .. <i>Ber.</i> , 1934, 65 , 211-214. |
| 2. J. A. V. Butler | .. <i>Trans. Faraday Soc.</i> , 1924, 19 , Part III, p. 729. |
| 3. Ewing and Rosenhain | .. <i>Proc. Roy. Soc.</i> , 45 , p. 85. |

CHEMOTHERAPY OF BACTERIAL INFECTIONS

IX. Synthesis of Some Sulphathiazole Derivatives

BY K. GANAPATHI

(Department of Chemotherapy, Haffkine Institute, Parel, Bombay)

Received April 1, 1943

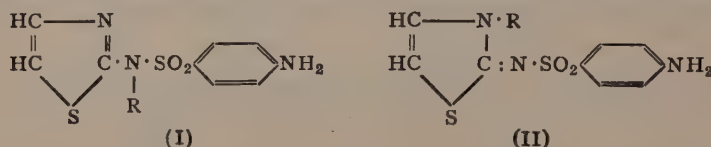
(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.Sc.)

CONSIDERABLE attention is being given in recent times to the discovery of sulphanilamide derivatives for the treatment of infections of the typhoid-cholera-dysentery group. A drug to be ideal for these intestinal infections should, besides possessing very strong bacteriostatic and bactericidal action against the organism concerned, remain localised in the intestine with little of it being absorbed from there into the blood stream. Such a drug should be harmless even with very high concentrations in the intestine because the toxic effects produced by the drugs are mainly the results of their high concentrations in the blood. Basing on this principle, Marshall *et al.*¹ brought forward sulphanilylguanidine as a drug suitable for the treatment of the intestinal infections. Though there are fairly good reports on the treatment of bacillary dysentery with this drug, it does not impress on us to be as excellent as sulphanilamide or sulphathiazole in their respective spheres of action (compare for example²). We attempted therefore to prepare other compounds which may fulfil the criteria mentioned above.

It has previously been reported³ from this laboratory that sulphathiazole protects mice against septicæmia due to *B. typhosum* and that it shows distinct bacteriostasis against *V. cholerae* *in vitro* in as low a concentration as 3 mg. per cent., while sulphanilamide even in 10 mg. per cent. shows no bacteriostasis. The disadvantage of this drug for our present purpose is that it is very rapidly absorbed from the intestine so that it is difficult to attain very high concentrations of this in the intestine without increasing correspondingly the concentration in the blood to dangerous limits. So we sought to prepare derivatives of sulphathiazole of such a type that the original therapeutic activity may not be much impaired and at the same time its absorption from the intestine will considerably be reduced. The poor absorption of sulphaguanidine from the intestine which is alkaline in pH, appeared to us to be due to its insolubility in alkali and so we attempted to prepare derivatives of sulphathiazole of formula (I) or (II).

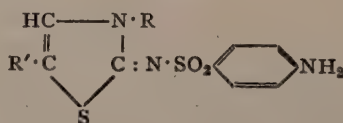
The other object in synthesising compounds of this type is to aid us in correlating chemotherapeutic activity with chemical constitution. Derivatives of sulphathiazole with alkyl substituents at positions 4 and/or 5 of the thiazole ring were previously reported.⁴ The compounds described here represent the third possibility of introducing further substituents in the molecule of sulphathiazole.

Sulphathiazole readily condensed with alkyl bromide or iodide (R. Hal) or sulphate in alkaline solution to yield a substitution product wherein the (N⁴-) amino group was found to be unsubstituted. The yields were better and the products much purer if the sodium salt of sulphathiazole was treated with the halide in alcohol. While methyl, ethyl, butyl, *iso*amyl and hexyl bromides or iodides readily condensed, *isopropyl*bromide was very reluctant to undergo the condensation under these conditions. β -Chloroethylamine and β -bromoethyldiethylamine did condense with sodium sulphathiazole



but the products obtained could not be crystallised. Ethylchloroacetate as well as ethyl α -chloroacetoacetate on condensation with sodium sulphathiazole yielded the same compound (No. 93); thus the acetyl group in the latter reagent appears to get eliminated in the process. The compounds prepared are listed in the table.

TABLE



Serial No.	R =	R' =	M.P. °C.	Molecular Formula	% Nitrogen	
					Found	Required
83	Methyl-	H	244-46	C ₁₀ H ₁₁ N ₃ O ₂ S ₂	15.3	15.6
84	Ethyl-	H	183-85	C ₁₁ H ₁₃ N ₃ O ₂ S ₂	15.2	14.8
85	<i>n</i> -Butyl-	H	186-88	C ₁₃ H ₁₇ N ₃ O ₂ S ₂	13.2	13.5
86	<i>iso</i> -Amyl-	H	201-3	C ₁₄ H ₁₉ N ₃ O ₂ S ₂	12.2	12.9
82	<i>n</i> -Hexyl-	H	156	C ₁₅ H ₂₁ N ₃ O ₂ S ₂	12.4	12.4
106	β -Hydroxyethyl-	H	154-56	C ₁₁ H ₁₃ N ₃ O ₅ S ₂	13.8	14.0
94	β -Ethoxyethyl-	H	150-52	C ₁₃ H ₁₇ N ₃ O ₄ S ₂	1.0	12.0
95	Acetonyl-	H	202	C ₁₂ H ₁₃ N ₃ O ₅ S ₂	12.9	13.0
93	Carbethoxymethyl-	H	184-85	C ₁₃ H ₁₅ N ₃ O ₄ S ₂	12.6	12.3
92	Methyl-	<i>iso</i> -Pr	157-60	C ₁₃ H ₁₁ N ₃ O ₂ S ₂	13.3	13.0

For the compounds obtained as above described, two structures (I) and (II) are possible. Because of the existence of the triad system, $-N=C-N\cdot R \rightleftharpoons R\cdot N-C=N-$, the compound (I) can easily isomerise to (II) and there are instances known in literature of such an isomerisation. On boiling the alkyl bromides with an alkaline solution of sulphathiazole, a low melting product is first obtained in many cases, which during the process of crystallisation is gradually transformed into one of higher melting point. We have not succeeded in isolating the lower melting ones in these cases (an instance wherein this has been done is reported in the next part) and it is difficult to assert that this is due to isomerisation since dimorphism is also well known among these compounds. After this work was completed, Hartmann and Druey⁵ have found that acetsulphanilylchloride condensed with 3-methyl-2-thiazolonimin to yield the same product obtained by methylating acetylsulphathiazole with dimethyl sulphate; this on hydrolysis yielded the methyl derivative (II, $R = Me$), m.p. 245–6°. On the other hand, *p*-nitrobenzenesulphochloride condensed with 2-methylaminothiazole and the product obtained on reduction yielded a compound, m.p. 109–10°, to be represented as (I, $R = Me$). Jensen⁶ has also reported the same. Druey⁷ has recently reported the preparation of a series of compounds of formula (II) by condensing 3-substituted thiazolonimids with *p*-nitrobenzenesulphochloride and reducing the resulting compound and also by condensing (N^4) acetylsulphathiazole with the alkyl halides and hydrolysing the resulting products. The products thus prepared appear to be identical with those reported by us here, though there are slight differences in the melting points (these compounds as a class frequently do not give sharp melting points). Thus we assign the structure (II) to the compounds obtained by us.

The compounds described here, excepting that number 92, have been tested in experimental plague infections in mice during December 1941–January 1942, according to the technique of Sokhey and Dikshit.⁸ The methyl derivative 83, showed therapeutic activity comparable to sulphathiazole. The ethyl compound, 84, gave only one survivor out of ten and the average survival time of the mice was slightly greater than that of the controls; so also was the case with the β -hydroxyethyl derivative, 106. All the others were inactive. The methyl derivative, 83, also showed good therapeutic effect in experimental streptococcal and pneumococcal infections in mice. Because of its sparing solubility in water (less than 0.5 mg. per cent.) its *in vitro* bacteriostatic effect could not be studied; however, it is interesting that this compound after oral administration to mice produces sufficient concentration in the blood to exert a pronounced therapeutic effect.

Experimental

Unless otherwise stated, the yields are all to be understood as good in the following experiments.

2-(p-Aminobenzenesulphonimido)-3-methyl thiazolone (II, R = Me).—To 2-sulphanilamidothiazole (50 g.) dissolved in sodium hydroxide (2.5 N, 160 c.c.) was added gradually under good shaking dimethyl sulphate (40 c.c.). A crystalline product began to separate. After good shaking it was allowed to stand for about one hour (the solution was distinctly alkaline), then filtered, the crystalline product triturated well with dil. sodium hydroxide, washed well and crystallised from alcohol. Yield, 46 g.

This compound could also be obtained by reacting sulphathiazole in alkaline solution or sodium sulphathiazole in alcohol with methyl iodide. In no case could the low melting isomer be obtained.

This compound was recovered unchanged after boiling with 4 N hydrochloric acid or 2.5 N sodium hydroxide for one hour.

2-(p-Aminobenzenesulphonimido)-3-butylthiazolone (II, R = Bu).—Sulphathiazole (12.4 g.) dissolved in sodium hydroxide (2.5 N, 40 c.c.) was boiled with butyl bromide (10 c.c.) or butyl iodide (8 c.c.) till there was no further increase in the quantity of the crystalline solid that separated (about 1 hour). It was cooled, the crystalline solid separated, washed well with alkali, then with water and crystallised from alcohol.

2-(p-Aminobenzenesulphonimido)-3-isoamyl thiazolone (II, R = isoamyl).—To sodium salt of sulphathiazole (13.7 g.) was added methyl alcohol (50 c.c.) followed by isoamyl bromide (10 c.c.), and the whole heated under reflux for about one hour and then allowed to stand overnight. The crystalline product that separated as such and also from the mother-liquors on dilution, was washed well with dil. alkali, then with water and crystallised from alcohol.

Similarly, the ethyl and hexyl compounds were* prepared by utilising ethyl iodide and hexyl bromide.

2-(p-Aminobenzenesulphonimido)-3-carbethoxymethylthiazolone (II, R = CH₂COOEt).—Sodium (1.2 g.) was dissolved in absolute alcohol (50 c.c.) and to this was added sulphathiazole (12.8 g.) and the mixture refluxed for 15 minutes. To the solution was added ethyl chloroacetate (8.0 g.) and the refluxing continued for about one hour more. After allowing it to stand overnight the product that had separated was filtered, rapidly washed with alkali, then with water and crystallised from alcohol.

The same compound was obtained when sodium sulphathiazole was condensed with ethyl α -chloroacetoacetate.

2-(p-Aminobenzenesulphonimido)-3-acetyl thiazolone (II, $R = CH_2COCH_3$).—The sodium salt of sulphathiazole (13.7 g.) was taken up in absolute ethyl alcohol (75 c.c.), chloroacetone (5 g.) was added and the mixture heated under reflux. A crystalline solid soon separated. The mixture was heated for about an hour more when the chloroacetone had completely disappeared. It was then filtered, the product washed with alkali, then with water and crystallised from alcohol.

2-(p-Aminobenzenesulphonimido)-3- β -hydroxyethyl thiazolone (II, $R = HO \cdot CH_2CH_2-$).—To sodium salt of sulphathiazole (13.7 g.) in methyl alcohol (20 c.c.) was added ethylene chlorhydrin (10 g.) and the mixture refluxed for about one hour. Further working up of this was as described in the previous cases.

I am indebted to Mr. C. V. Deliwala for the nitrogen estimations recorded here. I also thank Lt.-Col. S. S. Sokhey for his kind interest in these investigations.

Summary

The synthesis of various derivatives of sulphathiazole with alkyl and substituted alkyl substituents at the ring nitrogen of the thiazole nucleus has been described. Of these compounds only the methyl derivative showed good therapeutic activity in experimental streptococcal, pneumococcal and plague infections in mice.

REFERENCES

1. Marshall, Bratton, White and Litchfield *Bull. Johns Hop. Hosp.*, 1940, **67**, 163.
2. Firor and Poth .. *Ann. Surg.*, 1941, **114**, 663.
Poth, Knotts, Lee and Inui *Ibid.*, 1942, **44**, 187.
3. Rao and Ganapathi .. *Indian Med. Gaz.*, 1941, **76**, 78.
4. Ganapathi, Shirsat and Deliwala *Proc. Ind. Acad. Sci.*, 1941, **14 A**, 630.
———, Deliwala and Shirsat *Ibid.*, 1942, **16 A**, 126.
5. Hartmann and Druey .. *Helv. Chim. Acta*, 1941, **24**, 536.
6. Jensen, K. A. .. *Ibid.*, 1941, **24**, 1249.
Jensen and Thorsteinsson .. *C. A.*, 1941, **35**, 5109.
7. Druey, J. .. *Helv. Chim. Acta*, 1941, **24**, 226 E.
8. Sokhey and Dikshit .. *Lancet*, 1940, **1**, 1040.

CHEMOTHERAPY OF BACTERIAL INFECTIONS

X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-Diacetsulphanilylamidothiazole. A New Route to Sulphathiazole

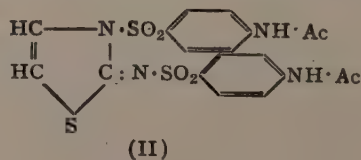
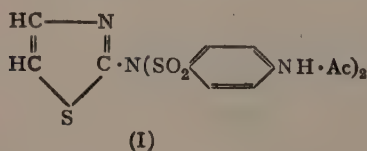
BY C. V. DELIWALA, K. GANAPATHI AND M. V. SHIRSAT

(From the Department of Chemotherapy, Haffkine Institute, Parel, Bombay)

Received April 1, 1943

(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.Sc.)

WHEN the condensation of 2-aminothiazole and acetsulphanilyl-chloride in molecular proportions is effected in the presence of pyridine, 2-acetsulphanilamidothiazole is produced in good yields. On the other hand, the use of inorganic basic condensing agents in the place of pyridine has now been found to yield different results. Tuda, Iticawa and So² have reported that the condensation of acetsulphanilylchloride with 2-aminopyridine in acetone in the presence of sodium bicarbonate yields 2-acetsulphanilamidopyridine; Bobranski and Eker² have obtained the same results by using sodium oxide in the place of sodium bicarbonate. But when the condensation of acetsulphanilylchloride with 2-aminothiazole was effected in the presence of sodium bicarbonate in acetone or aqueous solution, the product obtained was different from the expected 2-acetsulphanilamidothiazole. On crystallisation from alcohol it melted at 128–29°; it was insoluble in alkali but was hydrolysed to sulphathiazole by means of alkali or acid. The same product was obtained by condensing two molecules of acetsulphanilylchloride with one of 2-aminothiazole in pyridine or by the action of acetsulphanilylchloride on an alkaline solution of 2-acetsulphanilamidothiazole. On boiling this product, m.p. 128–29°, with alcohol for some time, it was quantitatively transformed into another, which turned yellow at 190° and charred at 225°. It was also insoluble in alkali and hydrolysed to sulphathiazole. These two compounds can be either dimorphic or isomeric. Though definite evidence against the first possibility has not yet been procured, we are inclined to believe that they are isomers to be represented by the two structures (I) and (II). Since a compound of structure (I) can be



expected to isomerise to one of structure (II) and not so easily *vice versa* for the obvious steric reasons, we suggest the structure (I) for the lower melting compound and (II) for the other. Jensen and Thorsteinsson,³ in a paper which is not accessible and the abstract of which contains no details, have described a compound of structure (II), m.p. 200–220° (turning yellow at 190°); this may quite possibly be identical with the higher melting isomer described here.

It is thus of interest to note that whereas in the presence of pyridine, the condensation of 2-aminothiazole with a molecular equivalent of acet-sulphanilylchloride yields 2-acetsulphanilamidothiazole, the use of sodium bicarbonate in the place of pyridine results in the bicondensation product (I) which is easily hydrolysed to sulphathiazole. We have investigated the latter reaction from the practical point of view of the manufacture of sulphathiazole since such a process has not so far been described. We are now satisfied that this is a very feasible method with many practical advantages. The condensation of 2-aminothiazole with two molecular equivalents of acet-sulphanilylchloride can be effected in fairly good yields in aqueous suspension in the presence of sodium bicarbonate, calcium or barium carbonate. Calcium carbonate is preferred because of its cheapness and also giving better yields. Another observation made of practical importance is that the yields are better if the solution of aminothiazole is added to the slurry of the sulphochloride. The hydrolysis of the bicondensation product to sulphathiazole proceeds smoothly in good yields. The advantages of this method of preparation of sulphathiazole are: (1) the sulphochloride can be used in the wet state after washing with water by decantation, (2) the use of the costly and now practically unobtainable good grade of pyridine is dispensed with, (3) the products obtained are cleaner and much less coloured and (4) the whole working time is very much shortened. We are engaged in effecting further improvements in this method and studying the reaction with other alky aminothiazoles.

Experimental

2-Diacetsulphanilylamidothiazole (I).—(1) To 2-aminothiazole (10 g.) dissolved in dry pyridine (50 c.c.) was added with good shaking crystallised acet-sulphanilylchloride (46 g.). After all of it was added, the mixture was warmed on the water-bath for about half an hour, cooled and then poured into cold water. The solid that separated was filtered off, triturated with dilute sodium hydroxide solution, filtered, washed and crystallised from alcohol; yield, 35.0 g. The condensation product obtained in colourless needles melted at 128–29° (Found: N, 11.4; $C_{19}H_{18}N_4O_6S_3$ requires

N, 11.3%). When this product was hydrolysed by boiling for one half hour with about 4 N hydrochloric acid and further worked up as usual, sulphathiazole was obtained in very good yields.

(2) To a solution of 2-acetsulphanilamidothiazole (7.2 g.) in sodium hydroxide (60 c.c. of 2.5 N) was added with cooling and good shaking finely powdered acetsulphanilylchloride (6.0 g.). The whole was kept well ground in a mortar and the solution maintained slightly alkaline if necessary by addition of alkali. After allowing to stand for some hours, the product was filtered off, washed with water and crystallised from alcohol; m.p. 127–29° (mixed m.p. with the foregoing sample being the same). Yield, about 10 g.

(3) The same product was obtained on condensing 2-aminothiazole with one or two molecular equivalents of acetsulphanilchloride in aqueous solution in cold in the presence of 2.5 molecular equivalents of sodium bicarbonate.

2-Acetsulphanilimido-3-acetsulphanilylthiazolone (II).—When the product, m.p. 127–29°, was boiled in alcohol for one to two hours, it was transformed into one of higher melting point; this product which is sparingly soluble in alcohol, after repeated crystallisations from alcohol, was obtained in colourless needles which turns yellow at 190° and chars at 225° (Found: N, 11.3; $C_{19}H_{19}N_4O_6S_3$ requires N, 11.3%).

Preparation of Sulphathiazole.—The acetsulphanilylchloride prepared from acetanilide (1.0 kg.) and commercial chlorosulphonic acid (2.4 l.), was washed free from acid with water and suspended in water (8 to 10 l.). In case the solution was acidic, it was neutralised with calcium carbonate and then a further quantity of calcium carbonate (500 g.) was added and stirred well. A solution of crude 2-aminothiazole (250 g.) in water (4 l.) was slowly run in with good stirring. There was a vigorous evolution of carbon dioxide and the stirring was continued till it practically subsided. After allowing it to stand overnight, the solid was filtered off, triturated with dilute hydrochloric acid to decompose the excess of calcium carbonate and then washed with water (a sample of the condensation product on crystallisation from ethyl alcohol had m.p. 128–29°). The solid obtained was hydrolysed as usual by boiling with about 5 N hydrochloric acid or about ten per cent. sodium hydroxide. On neutralising the filtrate, sulphathiazole was thrown out. This was collected and recrystallised from boiling water (charcoal). The yield of the product obtained in colourless needles was about 250 g. and this can doubtless be improved.

We thank Lt.-Col. S. S. Sokhey, Director, for his keen interest in these investigations.

Summary

2-Aminothiazole condensed with acetsulphanilylchloride in aqueous solution or suspension in the presence of sodium bicarbonate, calcium carbonate or barium carbonate to yield 2-diacetsulphanilylamidothiazole, m.p. 128–29°; the same product is also obtained by condensing 2-aminothiazole with two molecular equivalents of acetsulphanilylchloride in pyridine or by condensing 2-acetsulphanilamidothiazole with acetsulphanilylchloride in alkaline solution. This compound on boiling with alcohol isomerises into 2-acetsulphanilimido-3-sulphanilylthiazolone. These two products are hydrolysed by acid or alkali to sulphathiazole in good yield. A process of preparation of sulphathiazole is described.

REFERENCES

1. Tuda, Iticawa and So .. *J. Pharm. Soc. Japan*, 1939, **59**, 213 ; *C. A.*, 1939, **33**, 8201.
2. Bobrabski and Eker .. *J. Applied Chem. U.S.S.R.*, 1940, **13**, 1637 ; *C. A.*, 1941, **35**, 3986.
3. Jensen and Thorsteinsson .. *Dansk. Tids. Farm.*, 1941, **15**, 41 ; *C. A.*, 1941, **35**, 5109.

FLUORESCENCE REACTIONS WITH BORIC ACID AND *o*-HYDROXY-CARBONYL COMPOUNDS, AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY

Part II. Detection of $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ in Aromatic Compounds
containing C, H and O only

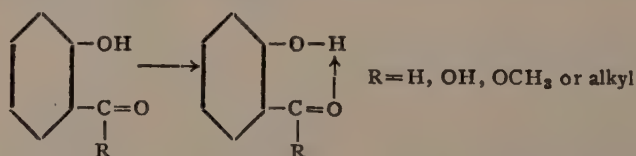
BY K. NEELAKANTAM, L. RAMACHANDRA ROW AND V. VENKATESWARLU
(From the Department of Chemistry, Andhra University, now at Madras)

Received October 14, 1943

It is well known that a hydroxyl ortho to the carbonyl group in aromatic

compounds, $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$, exhibits certain peculiarities, viz., that it is not

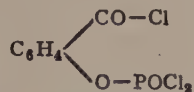
readily methylated and that it is less phenolic than when it is present in other positions. This behaviour has been observed not only with the simpler compounds such as resacetophenone, salicylic acid, etc., but also with the hydroxy-flavones, -flavonols, -flavanones, -chromones, -chalkones, -xanthenes, and -anthraquinones containing this group. These peculiarities have been ascribed to the existence of chelation between the hydroxyl hydrogen and the carbonyl oxygen thus:



leading to a diminution of ionisability of the phenolic hydrogen atom and also causing fixation of the double bonds. When the hydroxyl is in the meta or the para position to the carbonyl it behaves in the normal manner. Consequently the qualitative detection of the presence of a hydroxyl ortho to the carbonyl group is of considerable interest.

No attempt seems to have been made in the past to develop a general reaction for the detection of this group in various types of compounds. However, a few reactions which distinguish ortho-hydroxy carbonyl compounds from the meta- and para-compounds have been recorded and these could be utilised, though to a limited extent for this purpose.

Anschtütz¹ found that while the, *o*-, *m*-, and *p*-hydroxy benzoic acids themselves reacted with phosphorous pentachloride yielding the phosphorous oxychloride derivative of the phenolic carboxylic acid chloride of the following type:



ortho-hydroxybenzoic acids in which the second ortho position to the hydroxyl is already occupied give the free acid chlorides. Obviously, the reaction is of no value for detecting the presence of the ortho-hydroxy-carbonyl group in the simple unsubstituted hydroxy-benzoic acids. However, it could be employed, for example, with *o*-cresol-carboxylic acids.

Jean-Renaud² found that only esters of *o*-hydroxybenzoic acids yield with hydroxylamine and alkali in aqueous solution the corresponding hydroxamic acids, R-CO-NHOH, while the *m*- and *p*-compounds do not. Since the hydroxamic acids can be readily detected by means of the characteristic property which they possess of yielding a red or violet colour with ferric chloride, this difference could be utilised to distinguish the three types of hydroxy acids. However, it fails with the ester of β -naphthol- β -carboxylic acid, and Angelli and Castellana³ showed that if an alcoholic solution is employed, the ester of *m*-hydroxybenzoic acid also gives the hydroxamic acid. In this connection it is of interest to note that among the unsubstituted *o*-, *m*-, and *p*-hydroxybenzoic acids the ortho acid can be easily and directly distinguished by means of its colour reaction with ferric chloride. While the ortho compound yields a violet colour, the *m*-, and *p*-compounds give none. It may, however, be pointed out that substitution brings about a marked change in the colour obtained with the ferric chloride as, for example, in the case of 5-nitro-salicylic acid which yields a red colour and hence the ferric chloride colour reaction is not a sure test for the *o*-hydroxybenzoic acids.

A third reaction distinguishing the *o*-hydroxy-carboxylic acids from the *m*-, and *p*-acids has been reported by Nölting.⁴ Anilides of the ortho acids on treatment with dimethylaniline and phosphorous oxychloride yield compounds of the malachite green series whereas those of the *m*- and *p*-compounds yield derivatives of dialkyl-amido-benzophenones.

With regard to the hydroxy-ketones Pfeiffer *et. al.*⁵ found that while carbonyl compounds and *m*- and *p*-hydroxy-carbonyl compounds yielded with stannic chloride additive compounds, in the presence of an ortho-hydroxyl internally complex (chelate) compounds were obtained. The latter compounds are closely related to the tin lakes and are coloured unlike the additive compounds.

In the group of the hydroxy-anthraquinones, Dimroth *et al.*⁶ found that

the α -hydroxy compounds containing the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group gave on treatment with boracetic acid in acetic anhydride solution characteristic colour changes, in many cases with fluorescence, due to the formation of boracetate complexes (chelation) involving the hydroxyl and carbonyl and that when the hydroxyl was not in the ortho position to the carbonyl only acetylation of the former occurred. Brass *et al.*⁷ utilised this reaction for proving the absence of *l*-hydroxyl in the dihydroxyphenanthraquinone (2 : 4) they had prepared.

Feigl and Krumholz⁸ observed that boric acid itself reacts with α -hydroxy-anthraquinones dissolved in concentrated sulphuric acid yielding characteristic colour changes which can be used either for the detection of boric acid or the α -hydroxyanthraquinones. These authors explained these colour changes as due to the formation of inner complex (chelate) boric esters or of similar boric-sulphuric acid esters involving the ortho hydroxyl and the carbonyl group. From the data given by Meyer⁹ it is clear that generally in the absence of a hydroxyl ortho to the carbonyl group, no prominent colour changes occur on the addition of boric acid. However, a few exceptions are known. 2 : 3-dihydroxy-anthraquinone gives a colour change, though not a prominent one (red-brown to brown) on adding boric acid, but it does not contain a hydroxyl ortho (α) to the carbonyl group, while 1 : 3-dihydroxy- and 1 : 4 : 5 : 8-tetrahydroxy-anthraquinones fail to give a colour change on adding boric acid though they contain the α -hydroxyl.

Rangaswami and Seshadri¹⁰ showed that Wilson's boric-citric acid colour test is quite useful for the detection of the presence of a 5-hydroxyl in hydroxy-flavones and -flavonols and that a positive reaction is given by the methyl ethers also. Similar results were obtained with the *o*-hydroxy-chalkones and their methyl ethers. However, the 5-hydroxy-flavanones, naringenin and hesperetin, and the simpler *o*-hydroxy compounds, salicylic acid and resacetophenone fail to give the test. These authors pointed out that for a compound to yield a positive reaction the molecule should contain: (1) a keto-group, (2) an ortho hydroxyl or methoxyl and (3) an external double bond in conjugation with the C=O. This reaction is obviously

limited to those compounds containing the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group in which there is present in addition an external double bond in conjugation with the

C=O as in the case of 5-hydroxy-flavones, -flavonols and the 2-hydroxy-chalkones.

To the above may be added the ferric chloride colour reactions for the *o*-hydroxy-carbonyl compounds, acids, aldehydes and ketones which serve to a limited extent to distinguish the *o*- from the *m*- and *p*-compounds.

It is clear from the above that the available reactions for the detection

of the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group have been developed with reference to particular types of compounds and have consequently a limited range of applicability.

In a previous communication¹¹ which may be regarded as Part I of this series, Neelakantam and Row reported that addition of boric acid to solutions of the *O*-hydroxy-carbonyl compounds in concentrated sulphuric acid, except in a few cases, brought about either a marked intensification or a change in colour of the fluorescence exhibited by them in daylight or under the ultra-violet lamp. In some cases fluorescence appeared only on the addition of boric acid, the solutions (H_2SO_4) of the compounds themselves being non-fluorescent. These results were given not only by the simpler compounds such as salicylic acid, resacetophenone, etc., but also by most of the 5-hydroxy-flavones, -flavonols and -flavanones examined. In the

absence of the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group no fluorescence effects (*loc. cit.*) were observed except in one case (3:7-dihydroxy-flavone). These authors suggested that the reaction might serve for the detection of this group. It was, however, pointed out by them that a negative result does not necessarily indicates the absence of this group.

Since the previous work was published several other *o*-hydroxy-carbonyl compounds became available as a result of synthetic work done in our laboratories and it was felt desirable to examine the scope of this fluorescence

reaction as a general reaction for the detection of the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group in aromatic compounds. The present investigation is confined to compounds containing carbon, hydrogen and oxygen only. Feigl (*loc. cit.*) examined the colour reactions of the α -hydroxyanthraquinones with boric acid in daylight only and hence the few available compounds of this series were included in the present investigation. In all twenty-six compounds including some

o-hydroxychalkones recently synthesised in our laboratory have now been examined. Further, a variety of aromatic compounds containing the hydroxyl and carbonyl groups in other than the ortho position to each other and also those in which the hydroxyl or the carbonyl is absent have been examined to elucidate the limitations of the reaction.

Experimental

Solutions.—The boric acid solution and the solutions of the substances under investigation were prepared as described already.¹¹

Procedure.—The procedure adopted was also identical with the one previously described.

Results.—The colour of the fluorescence obtained with the *o*-hydroxy-carbonyl compounds is recorded below. The results obtained with compounds in which the two groups are not ortho to each other and also those in which one of them is absent are also recorded in order to test the specific nature of the reactions.

o-Hydroxy-ketones.—2-Hydroxy-6-methoxy-acetophenone gave a bright yellow and 2-hydroxy-4:6-dimethoxy-acetophenone a greenish yellow fluorescence with boric acid under the lamp. 2-Hydroxy-3:6-dimethoxy-acetophenone and ω -methoxy-phloracetophenone gave no fluorescence with boric acid even under the lamp. With all these compounds the blanks exhibited no fluorescence either in daylight or under the lamp.

o-Hydroxy-aldehydes.—2:4-Dihydroxy-6-methyl-benzaldehyde gave a bright greenish yellow and 2-hydroxy-4-methoxy-6-methyl-benzaldehyde a greenish yellow fluorescence with boric acid under the lamp. With the two compounds no fluorescence was obtained either in daylight or under the lamp in the blank test. 2-Hydroxy-4:6-dimethoxy-benzaldehyde, however, gave a pale yellow fluorescence in the blank test and a deeper yellow fluorescence with boric acid under the lamp.

o-Hydroxy-carboxylic acids and esters.—Atranorin and ethyl rhizonate gave no fluorescence in the blank test but with boric acid they gave a pale blue fluorescence under the lamp. Montagnetol and lecanoric acid gave a pale violet fluorescence under the lamp even without boric acid and on its addition this became deeper in both cases. The methyl ester of karanjic acid gave a pale blue fluorescence in the blank and a deeper blue with boric acid under the lamp.

o-Hydroxy-chalkones.—2:4:3':4'—Tetrahydroxy-chalkone (butein) dissolved in sulphuric acid gave a green fluorescence visible in daylight itself and on treatment with boric acid, there was appreciable increase in its intensity; the blank appeared greenish yellow under the lamp and with boric

acid a deeper greenish yellow. 2:4-Dihydroxy-chalkone gave a pale greenish yellow fluorescence in the blank and a deeper greenish yellow with boric acid under the lamp. 2:4:4'-Trihydroxy-3'-methoxy-chalkone gave an yellow fluorescence with boric acid under the lamp and none without it; in daylight no fluorescence was obtained with or without boric acid.

The following chalkones recently synthesised by Seshadri *et al.* (unpublished work) gave no fluorescence with or without boric acid in daylight or under the lamp :—

2:6-Dihydroxy-, 2:4'-dihydroxy-6:3'-dimethoxy-, 2:5:4'-trihydroxy-6:3'-dimethoxy-, 2-hydroxy-3:6-dimethoxy-, 2-hydroxy-3:6:4'-trimethoxy-, 2:4'-dihydroxy-3:6:3'-trimethoxy-, and 2-hydroxy-5:6:3':4'-tetramethoxy-chalkones.

α-Hydroxy-anthraquinones.—Quinizarin gave a pale yellow fluorescence in daylight itself without any boric acid and on its addition it was deepened; there was no appreciable colour change with the boric acid. The blank gave an orange-yellow fluorescence under the lamp and with boric acid this became deeper yellow. Alizarin, quinalizarin and *rheum*-emodin (2-methyl-4:5:7-trihydroxy-anthraquinone) gave no fluorescence with or without boric acid in daylight or under the lamp. In these cases prominent colour changes occurred on the addition of boric acid. Alizarin gave a pale pink solution which became violet on adding boric acid, with quinalizarin the change was from violet to blue and in the case of *rheum*-emodin from orange to violet-red.

$$\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \\ \text{—C—C—C—} \\ | \quad | \end{array}$$

Compounds in which the —C—C—C— group is absent.—The following compounds gave no fluorescence with or without boric acid in daylight or under the lamp :—

p-Hydroxy-benzaldehyde, vanillin, isovanillin, protocatechuic aldehyde, benzoin, benzil, *α*-naphthol, 5:6:3':4'-tetramethoxy-flavanone, anisic acid and gallic acid.

In the following cases the solutions of the substances in concentrated sulphuric acid gave fluorescence under the lamp but on the addition of boric acid there was no change in intensity or in colour :—

m-, and *p*-Hydroxy-benzoic acids, mandelic acid, benzophenone, phthalic acid, *β*-naphthol and 3-methoxy-7-hydroxy-8-methyl-flavone.

Other compounds examined for negative evidence were the following :—

Benzilic acid, umbelliferone, 4-methyl-, 5-methyl-, 4:8-dimethyl-, and 8-allyl-umbelliferone; 2-methyl-3-methoxy-7-hydroxy-, and 2-methyl-3-

methoxy-7-allyloxy-chromone, and 6:8-diallyl-7-hydroxy-flavone. All these gave fluorescence when dissolved in sulphuric acid even in daylight but addition of boric acid produced no change.

7-Methoxy-3-hydroxy-flavone, however, behaved in an exceptional manner. Its solution in concentrated sulphuric acid exhibited a light greenish blue fluorescence in daylight which on the addition of boric acid became a bright blue; under the lamp it was bright green in the blank and deep blue with boric acid.

Discussion

In the case of the *o*-hydroxy-ketones, -aldehydes, and -acids, the results now obtained generally support the conclusions reported in the previous communication (*loc. cit.*). Among the compounds now ex-

mined also there are a few cases in which though the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group is present negative results are obtained. Among the simpler *o*-hydroxy-carbonyl compounds it appears that when the 3-position is occupied either by a methyl or a methoxy group as in 3-methylresacetophenone, 2-hydroxy-3:6-dimethoxy acetophenone and 3-methyl-4-methoxy-2-hydroxybenzoic acid, no fluorescence is observed with boric acid either in daylight or under the lamp. ω -Methoxy-phloracetophenone also gives a negative result with boric acid.

In the group of the *o*-hydroxy-chalkones, out of the ten cases examined positive fluorescence effects were obtained only with three and it is interesting to note that all these are derived from β -resacetophenone. A comparison of the results obtained with the chalkones and the corresponding ketones shows that the behaviour of the two classes is not always parallel and while the ketones may exhibit the fluorescence effects the corresponding chalkones may not. Thus γ -resacetophenone itself yields positive results while the chalkones derived from it do not but 2-hydroxy-3:6-dimethoxy-acetophenone itself gives negative results and so also the chalkones derived from it. It may be stated in general that conversion of a ketone to a chalkone reduces the capacity to exhibit fluorescence.

The α -hydroxy-anthraquinones yield strongly coloured solutions when dissolved in concentrated sulphuric acid and even when diluted largely with the acid they do not give any fluorescence effects with boric acid except in the case of quinizarin. It appears that when addition of boric acid produces colour changes, no fluorescence effects are obtained.

Compounds which do not contain the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group gave negative results with boric acid, with one exception, in all the cases examined.

The results presented in this paper in conjunction with those already reported in Part I (*loc. cit.*) show clearly that a large number of compounds containing

the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group such as the *o*-hydroxy-acids, -ketones and -aldehydes; the 5-hydroxy-flavones, -flavonols and -flavanones; *o*-hydroxy-chalkones and α -hydroxy-anthraquinones give positive fluorescence effects with boric acid. However, there are cases in which though this group is present negative results are obtained. With the data available at present no general explanation could be given for these exceptions.

Among the compounds examined so far only in the cases of 3:7-dihydroxy-flavone reported in Part I and 7-methoxy-3-hydroxy-flavone in the present paper were fluorescence effects obtained with boric acid in the

absence of the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group. It is of interest to note in this connection that in the boric-citric acid test also both compounds gave a deep blue fluorescence but no colour.¹⁰ 7-Hydroxy-flavone itself gives a negative result in the fluorescence as well as in the boric-citric acid test. Obviously, therefore, the 3-hydroxyl group in 3:7-dihydroxy-flavone and in its 7-methyl ether is responsible for their exceptional behaviour in the fluorescence test. From the data available, therefore, it could be deduced that, with these two exceptions, a positive result with boric acid indicates the presence of the

$\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group in aromatic compounds containing carbon, hydrogen and oxygen only but the converse is not true.

It is evident that this reaction is of greater applicability than any so far reported in the literature. It is much more general than the others and is not confined to any one type of compounds. Further the test is very easily carried out and it does not involve further substitution as in Anschütz's method or preparation of derivatives as in Jean-Renaud's and Nölting's methods.

Conclusion

1. Addition of boric acid to aromatic compounds (C, H, and O only)

of various types containing the group $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$, dissolved in concentrated sulphuric acid generally produces a marked intensification or a change in colour of the fluorescence exhibited by them in daylight or under the lamp. In several cases the solution of the compound in sulphuric acid is itself non-fluorescent and fluorescence appears on adding boric acid.

2. In a few cases even when this group is present no fluorescence effects are obtained with boric acid.

3. 3:7-Dihydroxy-flavone and its 7-methyl ether are exceptions in that they give positive reactions with boric acid even though the above group is absent.

4. The fluorescence effects obtained with boric acid could be utilised

for the detection of the $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad | \quad || \\ -\text{C}-\text{C}-\text{C}- \\ | \quad | \end{array}$ group in various types of aromatic compounds containing carbon, hydrogen and oxygen only. A positive reaction indicates the presence of this group but the converse is not true.

5. This reaction is more general than all the others described in literature and is also easily carried out.

Further work is in progress.

The authors wish to express their thanks to Prof. T. R. Seshadri for valuable help rendered in the course of this investigation.

REFERENCES

1. Anschütz .. *Berichte*, 1897, **30**, 221; *cf. Brit. Chem. Abs.*, 1897, 219; *Annalen*, 1887, **239**, 314 and 333.
2. Jean-Renaud .. *Berichte*, 1889, **22**, 1273; *cf. Brit. Chem. Abs.*, 1889, 870.
3. Angelli and Castellana .. *Brit. Chem. Abs.*, 1909, **1**, 308.
4. Nölting .. *Berichte*, 1897, **30**, 2581; *cf. Brit. Chem. Abs.*, 1898, 143.
5. Pfeiffer *et al.* .. *Annalen*, 1913, **398**, 137-96; *cf. Brit. Chem. Abs.*, 1913, 104, (i), 879.
6. Dimroth *et al.* .. *Berichte*, 1921, **54 B**, 3020; *cf. Chem. Abs.*, 1922, **16**, 1766; *Annalen*, 1925, **446**, 97; *cf. Chem. Abs.*, 1926, **20**, 1052.
7. Brass *et al.* .. *Berichte*, 1930, **63 B**, 2621; *cf. Chem. Abs.*, 1931, **25**, 1242.
8. Feigl and Krumholz .. *Mikrochemie, Pregl-Festschrift*, 1929, 77.
9. Meyer .. *Nachweis und Bestimmung Organischer Verbindungen*, 1933, **2**, 300-13.
10. Rangaswami and Seshadri .. *Proc. Ind. Acad. Sci.*, 1942, **16 A**, 129.
11. Neelakantam and Row .. *Ibid.*, 1942, **15 A**, 81.

THE PHOTO-REDUCTION OF FERRIC CHLORIDE IN PRESENCE OF AQUEOUS ACETONE AND ANHYDROUS ETHER

BY MATA PRASAD AND P. R. BAVDEKAR

(From the Chemical Laboratories, The Royal Institute of Science, Bombay)

Received August 12, 1943

ALTHOUGH it is known that in admixed solutions with acetone ferric chloride is reduced in light (1) no work of a quantitative nature has yet been reported in literature. Some work, however, has been done on the photo-reduction of ethereal solutions of ferric chloride, but it lacks in thoroughness of treatment. Observations of a purely qualitative nature were made by Ben-rath (2), Puxeddu (3) and Spcier (4) using different regions of radiations as source of light. Later on, a quantitative study of the reaction was made by Puxeddu and Vodret (5) in sunlight as well as in arc light, but the method employed by them to estimate the amount of reduction is open to objection. They found that the reaction is of the first order and is completed in one hour. Further they found that the nature of the incident light has a marked effect on the reaction; at the same temperature the decomposition is much slower in arc light than in sunlight.

Talpade (6) has recently critically examined the applicability of various analytical reagents to estimate small quantities of ferrous iron in presence of large amounts of ferric iron and organic substance and has come to the conclusion that ceric sulphate is the only reagent which can be best employed for an unambiguous and direct measurement of a high degree of accuracy. The present investigation was therefore undertaken mainly with a view to obtain accurate quantitative data on the kinetics of the photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether using ceric sulphate method for the estimation of the amount of reduction from time to time. The various effects on the reaction due to the changes in the concentration of ferric chloride, temperature, wave-length and the intensity of light have been studied and the quantum efficiency of the reactions has been also measured in light of different spectral regions at different temperatures with different concentrations of ferric chloride solutions.

Experimental

The source of light was a Phillip's 1000-watt vertical type cinema projector lamp worked at a constant current of 4.2 amps. The reaction cell

was made of optically plane parallel quartz plates; its capacity was 4.5 c.c. and internal thickness 5 mm. It was cemented at the top to a thick glass plate with two holes through which passed siphon tubes ground to the holes in the plate. To the siphon tubes were attached pieces of India rubber tubing which were closed air tight.

The light filters were Kodak's wratten filters. The mean wave-length transmitted in each case was determined spectroscopically and was found to be as follows:—

Blue filter	4725 A.U.
Yellow filter	5975 A.U.
Red filter	6625 A.U.

Ferric chloride used was of A.R. quality obtained from B.D.H. It was dissolved in redistilled water with the addition of a certain amount of HCl in order to prevent the hydrolysis of ferric chloride (7) and also to stabilise the pH. Ethereal solutions of ferric chloride were prepared in Merck's extra-pure ether. Aqueous solutions of acetone were made by dissolving Merck's extra-pure quality acetone in redistilled water. These solutions were made in the dark and stored in air tight bottles which were always kept in a cool dry place.

After the elimination of heat radiations the parallel beam of light was incident on the reaction cell which was carefully screened from other radiations and was shaken from time to time to avoid the formation of "inner filters" (7). A Hilger thermopile connected to a Moll galvanometer recorded the intensity of the incident and the emergent beam of light. The absorbed energy was calculated from the galvanometer deflection differences for the reacting solution with and without ferric chloride, which were calibrated in terms of Hefner 100.

After insolating the mixture for a certain known interval, the cell was taken out of the thermostat and connected to a titration bottle and a wash bottle. On exhausting the air in the titration bottle the water from the wash bottle passed through the reaction cell to the titration bottle, thus draining the cell completely of its contents. The amount of reduction was determined by titrating the mixture against a standard solution of ceric sulphate with diphenylamine in sulphuric acid as an internal indicator in the presence of a few c.c. of syrupy phosphoric acid.

The results obtained are given in the following tables in which

a = the initial concentration of ferric chloride expressed in millimoles in 4 c.c. of the reaction mixture,

b = the initial concentration of acetone expressed in millimoles in 4 c.c. of the reaction mixture,

T = the temperature at which the reaction is studied,

I = the incident intensity in terms of galvanometer deflections,

λ = the wave-length of the exciting radiations in A.U.,

X = the amount of reduction of ferric chloride in millimoles in 4 c.c. of the reaction mixture,

t = the time of exposure in minutes, and

K = the unimolecular velocity constant.

TABLE I

Ferric Chloride and Aqueous Acetone

$b = 0.2764$; $T = 35^\circ$.

t	$a = 0.8604$		$a = 0.5736$		$a = 0.2868$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	6.12	1.151	4.05	1.190	2.12	1.228
120	12.06	1.170	7.96	1.190	4.18	1.247
180	17.86	1.164	11.88	1.177	6.26	1.228
240	23.58	1.161	15.88	1.180	8.28	1.228
300	29.36	1.159	19.66	1.174	10.26	1.220
360	35.19	1.158	23.49	1.164	12.24	1.209
480	46.44	1.156	31.18	1.171	16.06	1.204
600	57.60	1.155	38.70	1.170	19.80	1.194

TABLE II

Ferric Chloride and Anhydrous Ether

$T = 35^\circ$

t	$a = 0.9583$		$a = 0.4863$		$a = 0.2448$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	7.92	1.381	4.14	1.420	2.34	1.573
120	15.84	1.381	8.28	1.439	4.64	1.573
180	23.54	1.381	12.33	1.420	6.84	1.561
240	31.14	1.372	16.29	1.420	9.04	1.554
300	38.52	1.366	20.16	1.412	11.12	1.543
360	45.99	1.369	24.12	1.414	13.23	1.541
480	60.93	1.367	31.86	1.410	17.46	1.545
600	75.60	1.370	39.60	1.416	21.60	1.539

It can be seen from the above tables that the photo-reduction of ferric chloride in the presence of acetone and ether is not a zero-molecular reaction because the values of X/t decrease steadily as the reaction proceeds. If the reaction is of the first order, then the time required for the completion of the same fraction of the reaction carried out with different initial concentrations should be the same. Different values of X/a for reactions started with different initial concentrations were therefore calculated and are given in the following table:

TABLE III

t	X/a for acetone			X/a for ether		
	$a = 0.8604$	0.5736	0.2868	0.9583	0.4863	0.2448
60	0.0071	0.0071	0.0074	0.008	0.009	0.010
120	0.0140	0.0139	0.0146	0.016	0.017	0.019
180	0.0208	0.0207	0.0218	0.025	0.025	0.028
240	0.0274	0.0277	0.0289	0.032	0.034	0.037
300	0.0341	0.0343	0.0358	0.040	0.042	0.045
360	0.0409	0.0410	0.0427	0.048	0.050	0.054
480	0.0540	0.0544	0.0560	0.064	0.066	0.071
600	0.0669	0.0675	0.0690	0.079	0.081	0.088

It will be seen from the above table that for the same period of insolation the values of X/a are very nearly independent of the initial concentration of ferric chloride. The photo-reduction of ferric chloride in presence of acetone and ether, therefore, is a unimolecular reaction. This is confirmed by the facts that (i) the plot of $\log(a-X)$ against the time of insolation is a straight line, in all cases, and (ii) the values of the unimolecular velocity constants, given in Tables I and II, agree fairly well for a particular concentration of ferric chloride.

The mean values of the velocity constant for different initial concentrations of ferric chloride are given in the following table:

TABLE IV

a $K \times 10^4$	Acetone			Ether		
	0.8604 1.159	0.5736 1.177 Mean \rightarrow	0.2868 1.220 1.185	0.9583 1.373	0.4863 1.419 Mean \rightarrow	0.2448 1.554 1.449

It will be seen from the above table that the velocity constant decreases with increase in the concentration of ferric chloride, the deviations from the mean being beyond the experimental error.

The effect of temperature

The effect of temperature was examined by studying the kinetics of the reaction at 30° and 40° in addition to that studied at 35° in composite light. The results obtained are given in the following tables:

TABLE V
Ferric Chloride and Acetone

<i>t</i>	<i>a</i> = 0·8604		<i>a</i> = 0·5736		<i>a</i> = 0·2868	
	X × 10 ³	K × 10 ⁴	X × 10 ³	K × 10 ⁴	X × 10 ³	K × 10 ⁴
<i>Temperature 30°</i>						
60	5·40	1·036	3·42	0·998	1·94	1·113
120	10·71	1·036	6·72	0·998	3·74	1·074
180	15·75	1·023	9·99	0·985	5·40	1·062
240	20·97	1·027	13·27	0·988	7·16	1·065
<i>Temperature 40°</i>						
60	6·93	1·343	4·54	1·343	2·43	1·420
120	13·77	1·343	8·82	1·305	4·72	1·381
180	20·52	1·330	13·14	1·292	6·93	1·356
240	27·00	1·333	17·46	1·295	9·18	1·363

TABLE VI
Ferric Chloride in Ether

<i>t</i>	<i>a</i> = 0·9583		<i>a</i> = 0·4863		<i>a</i> = 0·2448	
	X × 10 ³	K × 10 ⁴	X × 10 ³	K × 10 ⁴	X × 10 ³	K × 10 ⁴
<i>Temperature 30°</i>						
60	7·34	1·266	3·92	1·343	2·15	1·458
120	14·49	1·266	7·52	1·305	4·23	1·439
180	21·51	1·253	11·25	1·292	6·21	1·420
240	28·35	1·257	14·85	1·295	8·19	1·420
<i>Temperature 40°</i>						
60	9·72	1·688	5·13	1·765	2·94	1·995
120	19·26	1·688	10·12	1·746	5·74	1·957
180	28·71	1·688	15·12	1·752	8·46	1·957
240	37·98	1·688	20·07	1·756	11·16	1·948

The effect of temperature on the velocity of the reaction is quite appreciable as will be seen from the following table which gives the mean values of the unimolecular velocity constants:

TABLE VII

<i>t</i>	Mean values of $K \times 10^4$ for					
	Acetone			Ether		
	$a = 0.9604$	0.5736	0.2868	0.9583	0.4863	0.2448
30°	1.030	0.992	1.078	1.260	1.309	1.434
35°	1.162	1.184	1.233	1.379	1.425	1.565
40°	1.337	1.309	1.380	1.688	1.755	1.964

The values of temperature coefficient between different temperatures have been calculated and they are given in the following table:

TABLE VIII

Temp. coeff. bet. temps.	Acetone			Ether		
	$a = 0.8604$	0.5736	0.2868	0.9583	0.4863	0.2448
30°-35°	1.128	1.193	1.144	1.094	1.089	1.091
35°-40°	1.150	1.105	1.119	1.224	1.231	1.225
30°-40°	1.298	1.319	1.280	1.340	1.341	1.370

It can be seen from the above table that the values of the temperature coefficient are almost constant within limits of experimental error and are practically independent of the initial concentration of ferric chloride. Also it will be seen in the case of ether that the temperature coefficient is a function of the temperatures between which it is calculated.

The low values of the temperature coefficient obtained in both the cases indicate that the photo-reduction of ferric chloride in presence of ether and acetone may be considered as a truly photochemical reaction.

The effect of wave-length

The effect of different wave-lengths was examined by studying the kinetics of the reaction in radiations filtered through the three filters described before. The results obtained are given in the following tables:

TABLE IX

Ferric Chloride and Acetone

$a = 0.9870$; $b = 0.2764$; $T = 35^\circ$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	0.92	1.535	0.72	1.190	0.63	1.074
120	1.80	1.535	1.42	1.190	1.25	1.055
180	2.67	1.522	2.08	1.177	1.86	1.049
240	3.55	1.526	2.75	1.180	2.47	1.055

TABLE X

Ferric Chloride and Ether

$a = 0.9583$; $T = 35^\circ$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	0.99	1.727	0.81	1.420	0.69	1.190
120	1.96	1.727	1.60	1.401	1.36	1.190
180	2.89	1.702	2.38	1.407	2.02	1.190
240	3.84	1.708	3.16	1.401	2.66	1.180

It can be seen from the above tables that the effect of the wavelength of the incident radiations on the velocity constant is quite marked. This has been brought out in the following table which gives the values of the unimolecular constant, taken from the above tables:

TABLE XI

TABLE XII

Filter	$K \times 10^4$ for		I	Acetone ($a = 0.972$)		Ether ($a = 0.9583$)	
	Acetone	Ether		$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
Blue	1.530	1.716	25.00	7.38	1.266	8.64	1.496
Yellow	1.184	1.407	21.15	6.12	1.074	7.20	1.266
Red	1.058	1.188	14.45	4.32	0.767	4.86	0.844

It will be seen that the values of the velocity constants in the three frequencies used decrease in the order blue > yellow > red, that is, the reaction takes place the most in blue light and the least in red. These results are as expected since the total energy of the absorbed light increases with the increase in the frequency of the exciting radiations.

The effect of intensity

The effect of the intensity of the incident light was examined by studying the reaction for one hour in composite light at 35°. The changes in the incident intensity were effected by changing the distance of the source of light from the reaction cell, thereby causing no change in the quality of the light. The results obtained are given in Table XII.

It will be seen that the effect of the intensity of the incident light is quite marked, the velocity constant is increased on increasing the intensity. The following table gives the ratios of the velocity constants and the corresponding ratios of the intensities, in which I_1 , I_2 and I_3 are the intensities and K_1 , K_2 and K_3 the corresponding values of the velocity constants:

TABLE XIII

		Acetone	Ether
$I_2/I_1 = 1.46$	$K_2/K_1 =$	1.40	1.50
$I_3/I_2 = 1.18$	$K_3/K_2 =$	1.18	1.18
$I_3/I_1 = 1.73$	$K_3/K_1 =$	1.65	1.77

It can be seen from the above table that the rate of reaction is directly proportional to the intensity of the incident light, the slight deviations being within the limits of experimental error. As the amount of absorbed radiation is directly proportional to the incident intensity (*cf.* Dhar, "The Chemical Action of Light"), these results show that the rate of reaction is directly proportional to the absorbed energy.

Quantum efficiency measurements

The quantum efficiency with different concentrations of ferric chloride for different wave-lengths was measured by using the same filters as used in the study of the kinetics of the reaction. The time of exposure of the reaction mixtures was one hour for all the measurements. The number of molecules changed during the period of exposure was calculated from the titration data and the number of quanta absorbed was determined from the measurement of the absorbed energy. The results obtained are given below:

TABLE XIV

Organic compound	<i>a</i>	Quantum efficiency at 35° for		
		4725 A.U.	5975 A.U.	6625 A.U.
Acetone	0.50	0.24	0.20	0.16
	0.10	0.38	0.30	0.24
	0.05	0.41	0.32	0.26
Ether	0.48	0.52	0.42	0.34
	0.12	0.76	0.61	0.49
	0.06	0.82	0.66	0.53

It will be seen from the above table that the values of the quantum yield in case of acetone are low, being in all cases less than 0.5; in ethereal solutions of ferric chloride, however, the yields are much higher. Further in will be seen that the quantum efficiency increases with dilution; the increase is fairly large on decreasing the concentration from 0.5 to 0.1 but is comparatively much less when it is decreased from 0.1 to 0.05. Also it can be seen that the values of the quantum yield decrease as the wave-length of the exciting radiation is increased. It is evident, therefore, that more molecules of ferric chloride are changed for every quantum of light absorbed, in light of a higher frequency than in that of a lower one.

The effect of temperature on the quantum yield was examined by determining the quantum yields at 30° and 40° in addition to those at 35°. The effect was studied only in blue light. The results obtained are given in the following table:

TABLE XV

Organic compound	<i>a</i>	Quantum efficiency for $\lambda = 4725$ A.U. at		
		30°	35°	40°
Acetone	0.50	0.22	0.24	0.29
	0.10	0.34	0.38	0.44
	0.05	0.37	0.41	0.48
Ether	0.48	0.47	0.52	0.64
	0.12	0.69	0.76	0.95
	0.06	0.74	0.82	1.02

It will be seen that the temperature has quite a marked effect on the quantum yield of the reaction. Also it can be seen that it is more marked for the same rise of temperature at a higher temperature. These results are analogous to those obtained in the study of the effect of temperature on

the velocity constant in case of ethereal solutions of ferric chloride. Such results have been obtained in many cases studied in this laboratory, but the only other case reported in the literature is the work of Kuhn (8). While studying the photo-decomposition of ammonia he obtained a 50 per cent. increase in the quantum yield for every 100 degree rise in temperature. He attributed this to the change in the kinetics of the reaction at higher temperatures.

Summary

1. The photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether is a unimolecular reaction.
2. The temperature and the frequency of the exciting radiations have a marked effect on the velocity constant of the reaction.
3. The rate of reaction is directly proportional to the intensity of the incident light.
4. The quantum yield of the reaction increases with dilution of ferric chloride, the temperature and the frequency of the exciting radiations and is of the order of 0.5 for acetone and 1.0 for ether.

REFERENCES

1. Baudisch, *Biochem. Zeit.*, 1918, **92**, 189.
2. *J. pr. Chem.*, 1905, **72**, 2207.
3. *Gazetta*, 1920, 501, 154.
4. *Trans. Farad. Soc.*, 1935, **31**, 1706.
5. *Gazetta*, 1922, **52**, 229.
6. *Proc. Nat. Acad. Sci.*, 1941, **2**, 1.
7. *J. Indian Chem. Soc.*, 1929, **6**, 827.
8. *Compt. rend.*, 1923, **177**, 956; 1924, **178**, 708; *J. chim. phys.*, 1926, **23**, 521.

INDEX TO VOL. XVIII (A)

AUTHORS' INDEX

- Asundi, R. K. .. Spectral and collision data of CO^+ and the dissociation energy of carbon monoxide, 8.
- Bavdekar, P. R. .. See Prasad and Bavdekar.
- Bhagavantam, S. .. Normal oscillations of the diamond structure, 251.
- Chelam, E. V. .. The normal vibrations in some typical cubic crystals, 257.
 .. Normal vibrations of crystal lattices : application of group theory, 283.
 .. Character tables for the atomic vibrations in some cubic crystals, 327.
 .. The frequency spectrum of the diamond lattice, 334.
- Chiplonkar, M. W., and Ranade, J. D. The brightness of the zenith sky during twilight, II, 121.
- Deliwala, C. V., Ganapathi, K., and Shirsat, M. V. Chemotherapy of bacterial infections, X, 360.
- Desai, T. V., and Guruswamy, S. Opacity changes in gel-forming mixtures during setting, II, 31.
- Ganapathi, K. .. Chemotherapy of bacterial infections, IX, 355.
 .. See Deliwala and others.
- Gautam, Lajja Ram, and Jha, J. B. Electrolytic solution pressure of copper wires under strain, 350.
- Guruswamy, S. .. See Desai and Guruswamy.
- Iyengar, K. S. K. .. A tauberian theorem and its application to convergence of Fourier series, 81.
 .. New convergence and summability tests for Fourier series, 113.
- Jha, J. B. .. See Gautam and Jha.
- Joshi, S. S., and Purushotham, A. Activation of nitrogen in the presence of mercury, 218.
- Kartha, A. R. Sukumaran, and Menon, K. N. The action of grignard reagents on benzopyrones, I, 28.
 .. Fixed oil from *Jatropha curcas* (Linn.), 160.

- Krishnan, R. S. .. Raman spectra of crystals and their interpretation, 298.
- Malurkar, S. L. .. Dynamics of thunderstorms, 20.
- Menon, K. N. .. See Kartha and Menon.
- Menon, P. Kesava .. On arithmetic functions, 88.
- Murti, P. Bhaskara Rama, and Seshadri, T. R. Chemical composition of *Calotropis gigantea*, I, 145.
- Neelakantam, K., and Rangaswami, S. Colorimetric estimation of boric acid with pentamethylquercetin, 171.
- Neelakantam, K., Row, L. Ramachandra, and Venkateswarlu, V. Fluorescence reactions with boric acid and *o*-hydroxycarbonyl compounds, and their application in analytical chemistry, II, 364.
- Pandya, Kantilal C., and Pandya, (Miss) Rashmi Bala K. The condensation of aldehydes with malonic acid, XV, 164.
- Pandya, (Miss) Rashmi Bala K. See Pandya and Pandya.
- Panse, T. B., and Paranjpe, A. S. A study of 'Carpasemine' isolated from *Carica papaya* seeds, 140.
- Pant, D. D. .. Luminescence spectra and vibrations in crystal lattices, 309.
- Paranjpe, A. S. .. See Panse and Paranjpe.
- Pasricha, B. R. .. Some integrals involving Humbert function, 11.
- Pillai, K. Sankara .. A note on Poisson distribution, 179.
- Prakash, Satya, and Rai, Ram Chandra Studies in blue perchromic acid, I, 1.
- Prasad, Mata, and Bavdekar, P. R. The photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether, 373.
- Purushotham, A. .. See Joshi and Purushotham.
- Rai, Ram Chandra .. See Prakash and Rai.
- Rajagopalan, S. .. Bacterial chemotherapy, I, II, III, 100, 104, 108.
- Ramachandran, G. N. .. Optical theory of chromatic emulsions and of the Christiansen experiment, 67.
- .. Fluctuations of light intensity in coronæ formed by diffraction, 190.
- .. Modes of atomic vibration in the fourteen Bravais lattices, 266.
- .. Modes of vibration of the hexagonal close-packed lattice, 341.

- Raman, C. V. .. The vibration spectrum of a crystal lattice, 237.
- Ranade, J. D. .. See Chiplonkar and Ranade.
- Rangaswami, S. .. See Neelakantam and Rangaswami.
- Rangaswami, S., and Seshadri, T. R. Chemical examination of Indian ergot of the Nilgiris, 206.
- Rao, N. S. Subba .. A further study of atmospherics during the monsoon period, 127.
- Rao, P. Suryaprakasa, and Seshadri, T. R. Pigments of cotton flowers, IX, 204.
- .. Some aspects of the biogenesis of anthoxanthins, 222.
- Row, L. Ramachandra .. See Neelakantam and others.
- Seshadri, T. R. .. See Murti and Seshadri.
- .. Chemical investigation of Indian fruits, IV, 201.
- .. See Rao and Seshadri.
- .. See Rangaswami and Seshadri.
- Shirsat, M. V. .. See Deliwala and others.
- Sunanda Bai, K. .. Interferometric studies of light scattering in binary liquid mixtures, I, 210.
- Ta-You Wu .. Excitation processes in the night sky and the aurora, 40.
- .. On Maris and Hulburt's ultraviolet light theory of auroræ and magnetic storms, 345.
- Venkateswarlu, V. .. See Neelakantam and others.

TITLE INDEX

- Aldehydes, condensation, with malonic acid, XV (Pandya and Miss Pandya), 164.
- Anthoxanthins, some aspects of the biogenesis (Rao and Seshadri), 222.
- Atmospherics during the monsoon period, a further study (Rao), 127.
- Auroræ and magnetic storms, on Maris and Hulburt's ultraviolet light theory (Ta-You Wu), 345.
- Benzopyrones, the action of grignard reagents, I (Karthi and Menon), 28.
- Boric acid and *o*-hydroxy-carbonyl compounds, fluorescence reactions, and their application in analytical chemistry, II (Neelakantam and others), 364.
- Boric acid, colorimetric estimation, with pentamethylquercetin (Neelakantam and Rangaswami), 171.
- Bravais lattices, fourteen, modes of atomic vibration (Ramachandran), 266.
- Calotropis gigantea*, chemical composition, I (Murti and Seshadri), 145.
- Carica papaya* seeds, 'Carpasemine' isolated from, a study (Panse and Paranjpe), 140.
- Chemotherapy, bacterial, I, II, III (Rajagopalan), 100, 104, 108.
- Chemotherapy of bacterial infections, IX (Ganapathi), 355 ; X (Deliwala and others), 360.
- Chromatic emulsions and the Christiansen experiment, optical theory (Ramachandran), 67.
- CO^+ , spectral and collision data, and the dissociation energy of carbon monoxide (Asundi), 8.
- Copper wires under strain, electrolytic solution pressure (Gautam and Jha), 350.
- Coronæ formed by diffraction, fluctuations in light intensity (Ramachandran), 190.
- Cotton flowers, pigments, IX (Rao and Seshadri), 204.
- Crystal lattices, luminescence spectra and vibrations (Pant), 309.
- Crystal lattices, normal vibrations : application of group theory (Chelam), 283.
- Crystal lattice, the vibration spectrum (Raman), 237.
- Crystals, Raman spectra, and their interpretation (Krishnan), 298.
- Crystals, some cubic, character tables for the atomic vibrations (Chelam), 327.
- Crystals, some typical cubic, the normal vibrations (Chelam), 257.
- Diamond lattice, the frequency spectrum (Chelam), 334.
- Diamond structure, normal oscillations (Bhagavantam), 251.
- Ergot, Indian, of the Nilgiris, chemical examination (Rangaswami and Seshadri), 206.

- Ferric chloride, the photo-reduction, in presence of aqueous acetone and anhydrous ether (Prasad and Bavdekar), 373.
- Fourier series, a tauberian theorem and its application to convergence of (Iyengar), 81.
- Fourier series, new convergence and summability tests for (Iyengar), 113.
- Fruits, Indian, chemical investigation, IV (Seshadri), 201.
- Functions, arithmetic (Menon), 88.
- Gel-forming mixtures, opacity changes, during setting, II (Desai and Guruswamy), 31.
- Humbert function, some integrals involving (Pasricha), 11.
- Jatropha curcas* (Linn.), fixed oil from (Karthi and Menon), 160.
- Lattice, hexagonal close-packed, modes of vibration (Ramachandran), 341.
- Light scattering in binary liquid mixtures, interferometric studies, I (Sunanda Bai), 210.
- Night sky and the aurora, excitation processes (Ta-You Wu), 40.
- Nitrogen, activation, in the presence of mercury (Joshi and Purushotham), 218.
- Perchromic acid, blue, studies (Prakash and Rai), 1.
- Poisson distribution, a note (Pillai), 179.
- Thunderstorms, dynamics (Malurkar), 20.
- Zenith sky, the brightness, during twilight, II (Chiplonkar and Ranade), 121.

